Des verres pas si désordonnées : implications pour les sciences de la terre et des matériaux

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Charles Le Losq, Rita Cicconi (IPGP)
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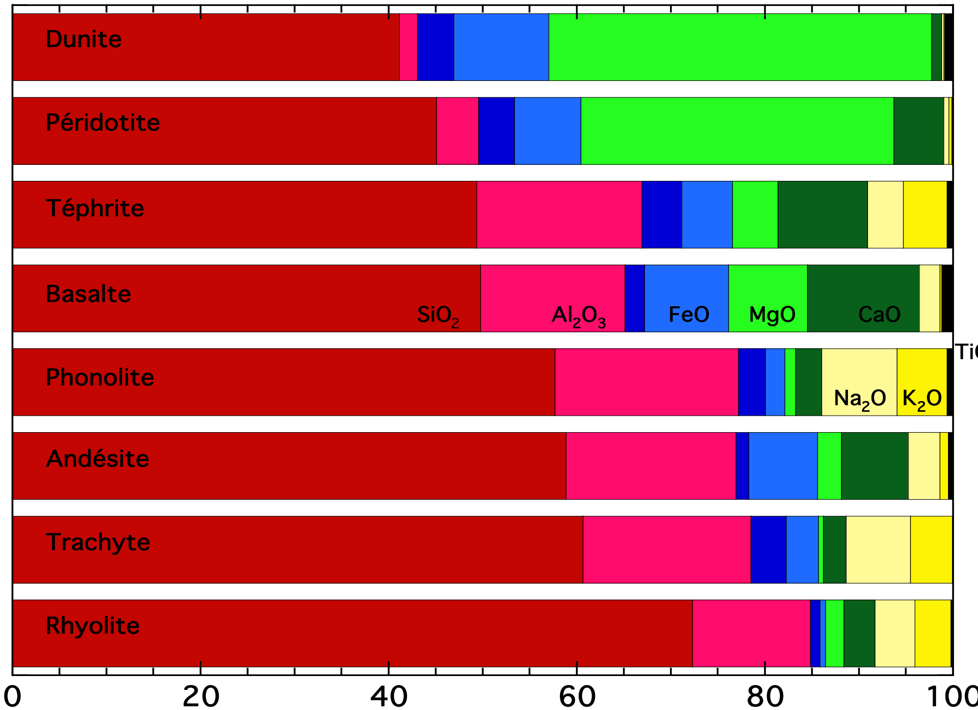
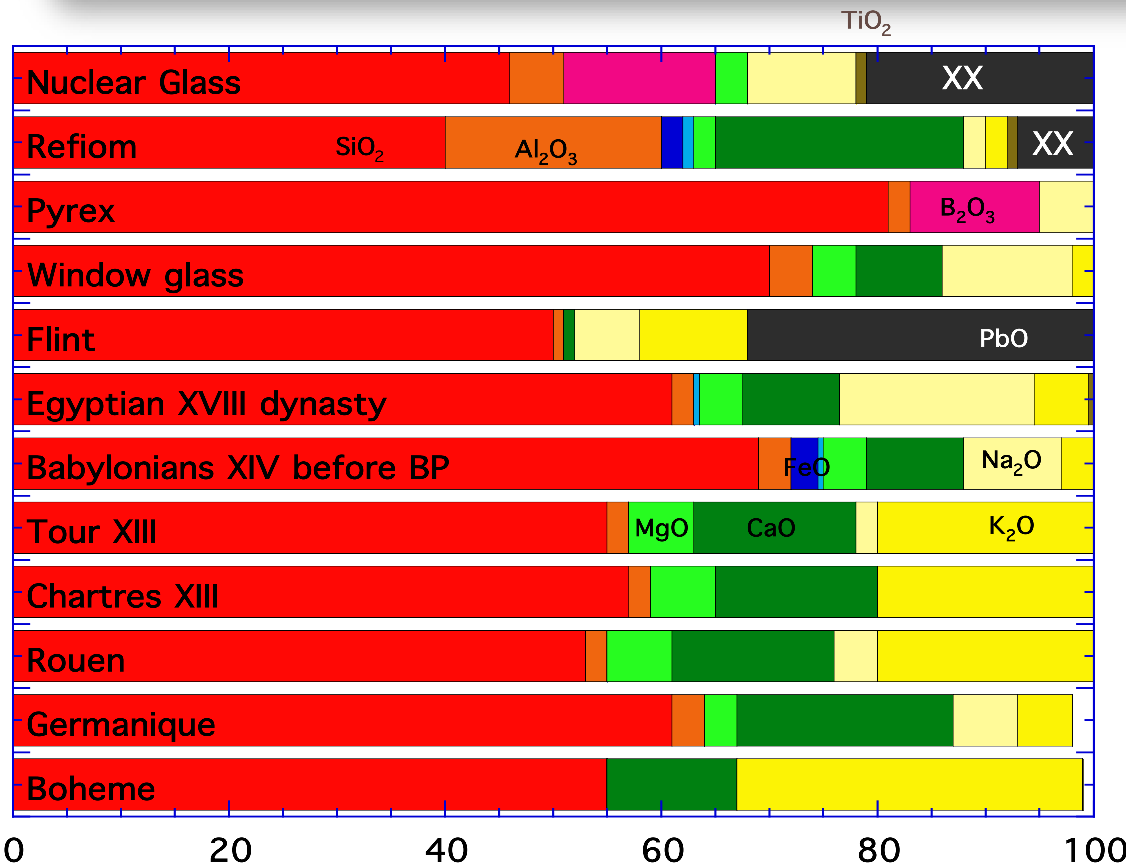
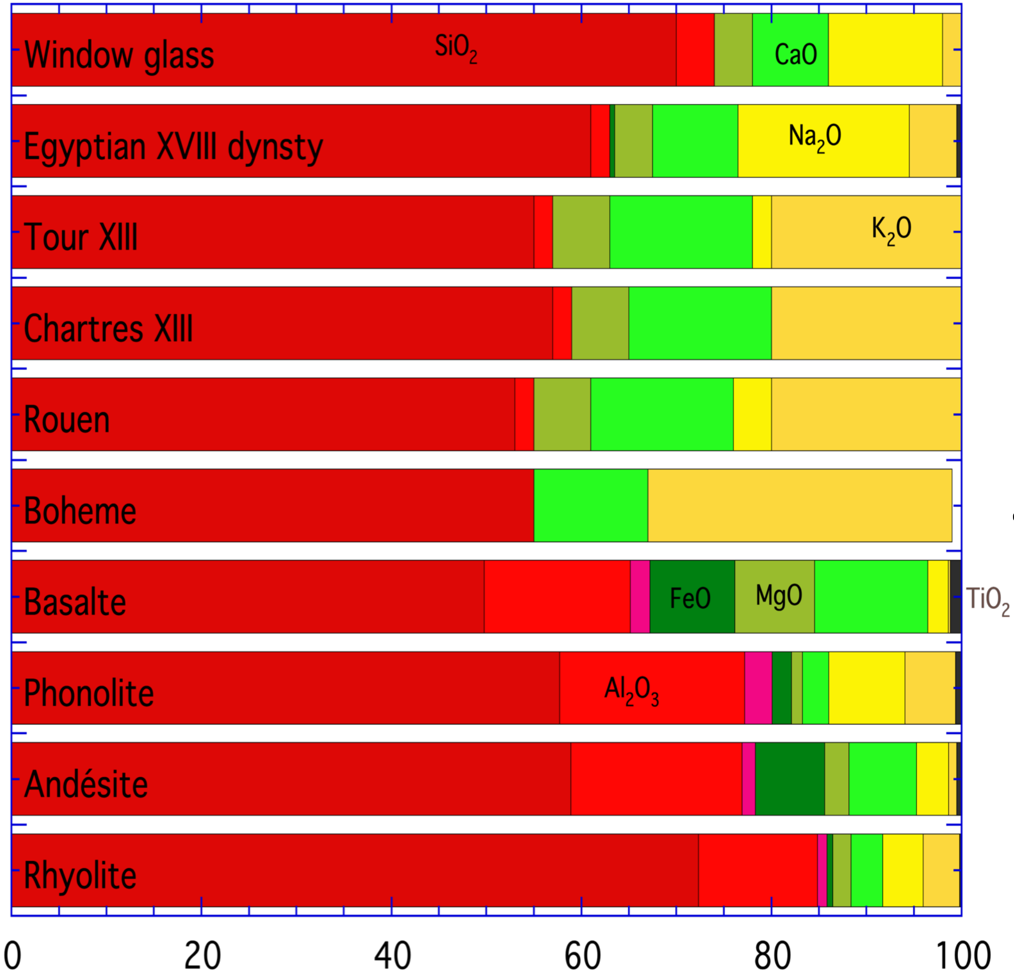
Natural lavas and magmas



Human glasses…..

Geomaterial





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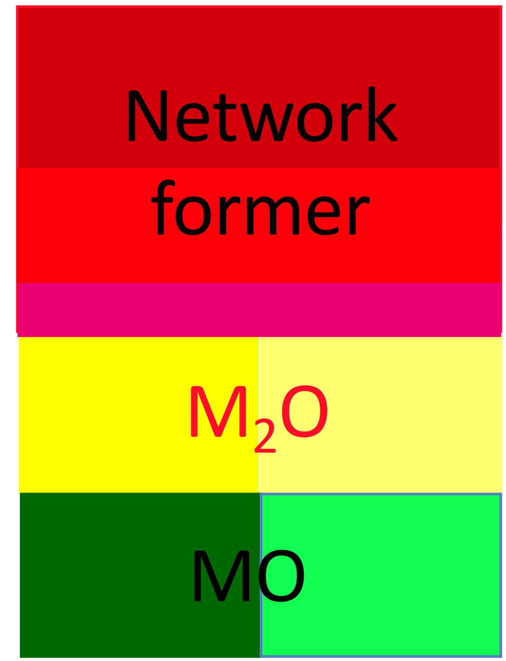
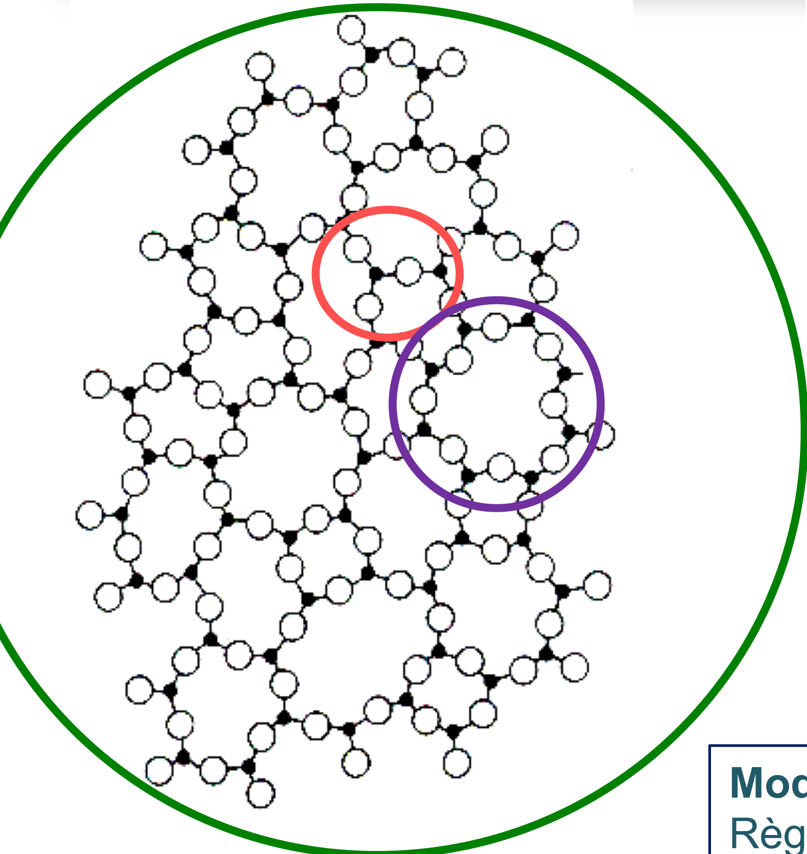


Properties versus Structure ?



Structure à courte distance :
– coordinence, longueurs de liaisons, angles de liaisons

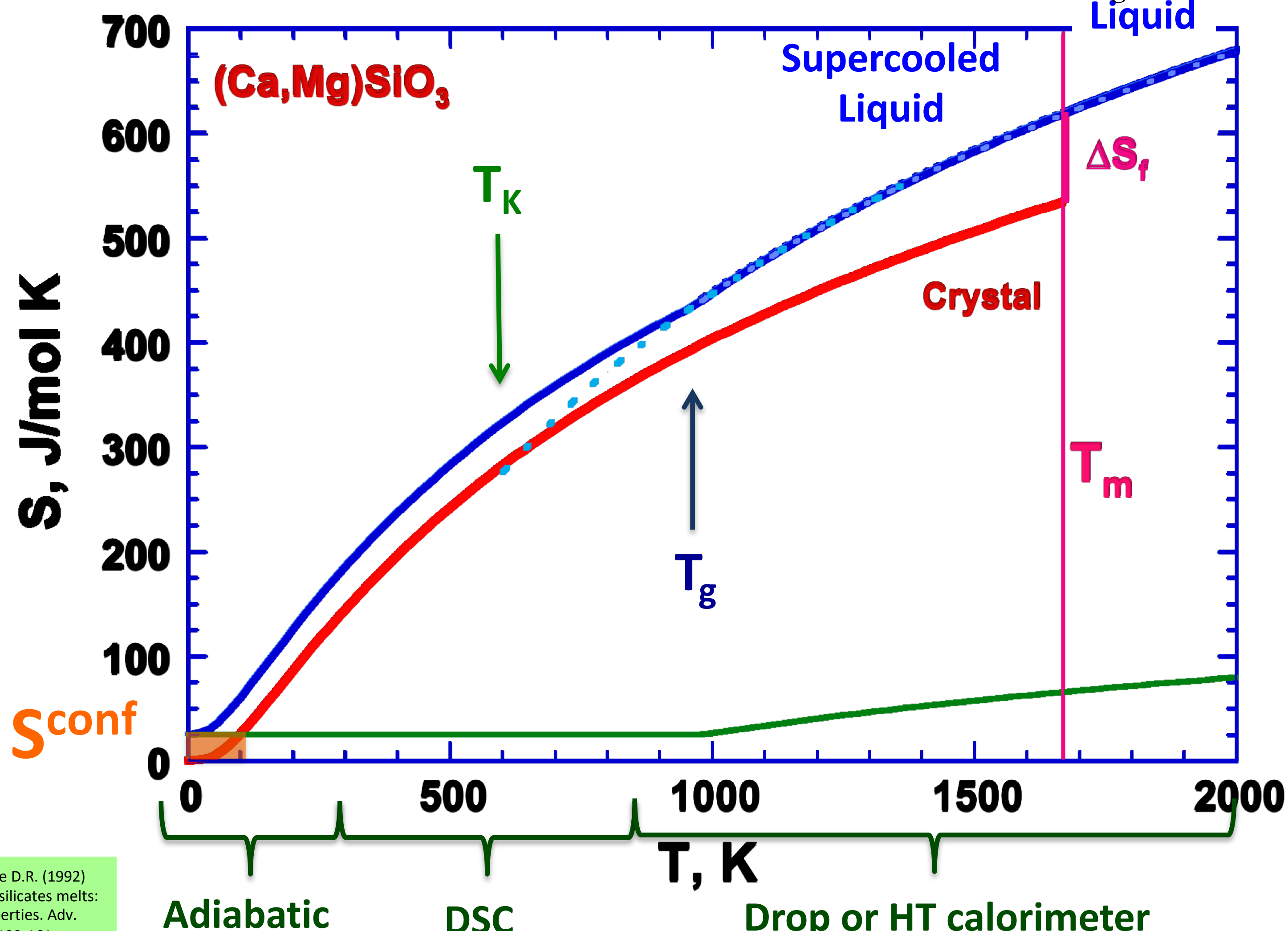
Structure à moyenne distance :
– angles entre les unités de base
– connectivité entre les unités de base (liaisons par sommet, arête …)
– dimensionnalité du réseau, anneaux

Structure à longue distance pas périodique !
– séparation de phase
– inhomogénéité

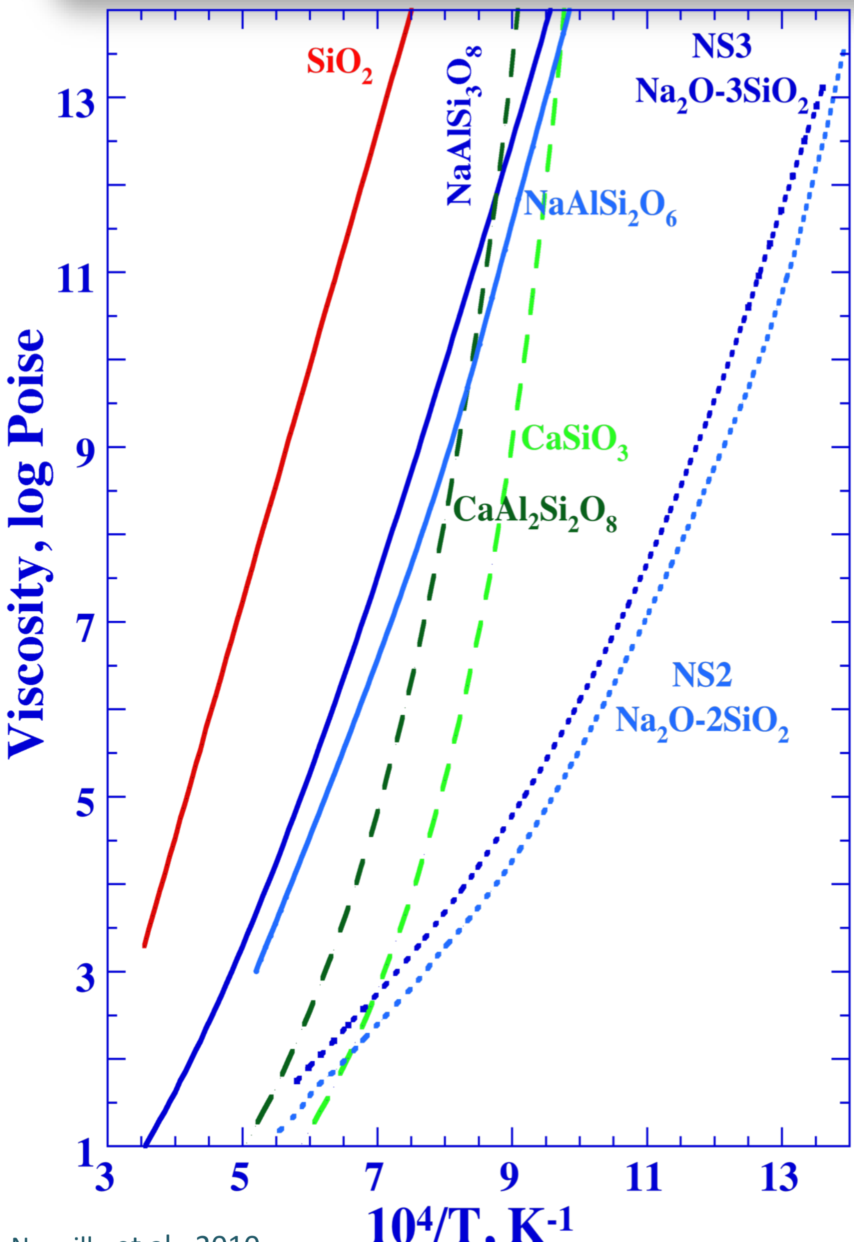
Modèle de Zachariasen (1932)
Règles pour la formation de verre

- 1. Pas d'atomes O liés à plus de 2 cations
- 2. La coordinence du cation est faible (3,4)
- 3. Les polyèdres d'O partagent des sommets, pas de faces ou d'arêtes
- 4. Pour les réseaux 3D, au moins 3 sommets doivent être partagés

$$S^{conf}(Tg) = \int_0^{Tm} \frac{Cp^{Crystal}}{T}.dT + \Delta S_f + \int_{Tm}^{Tg} \frac{Cp^{liquid}}{T}.dT + \int_{Tg}^{0} \frac{Cp^{glass}}{T}.dT$$



Richet P. and Neuville D.R. (1992) Thermodynamics of silicates melts: Configurational properties. Adv. Phys. Geochim., 10, 132-161.



Neuville et al., 2010

Arrhenius :

$$\eta(T) = A.\exp(E/RT)$$

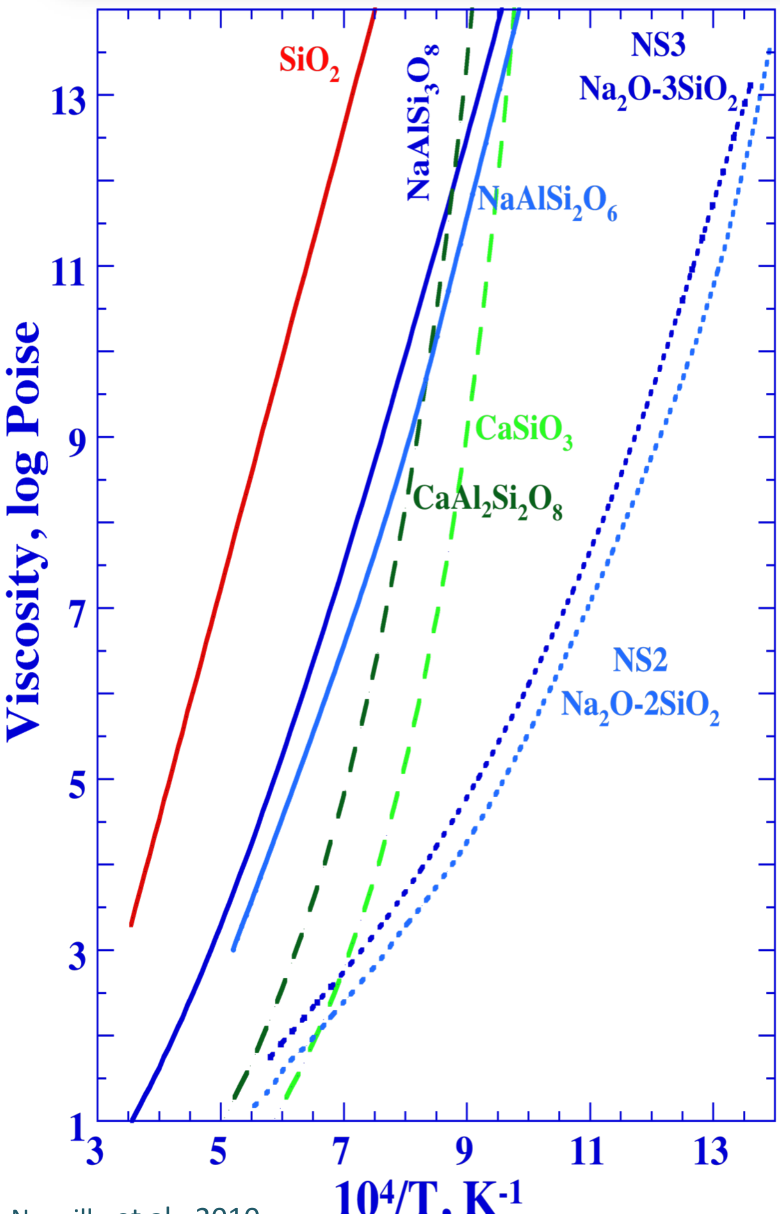
$\Leftrightarrow \log \eta = A + B/T$

Yes but only for SiO_2, GeO_2, $NaAlSiO_8$, $KAlSiO_8$ because activation energy change from 2000kJ/mol at 1000K up down 300kJ/mol at 1800K for NS3.

Need TVF equation

$$\log \eta = A_1 + B_1/(T-T_1)$$

But, just a fit .....



Neuville et al., 2010

$$\eta(T) = A_e.\exp[B_e/TS^{conf}(T)]$$

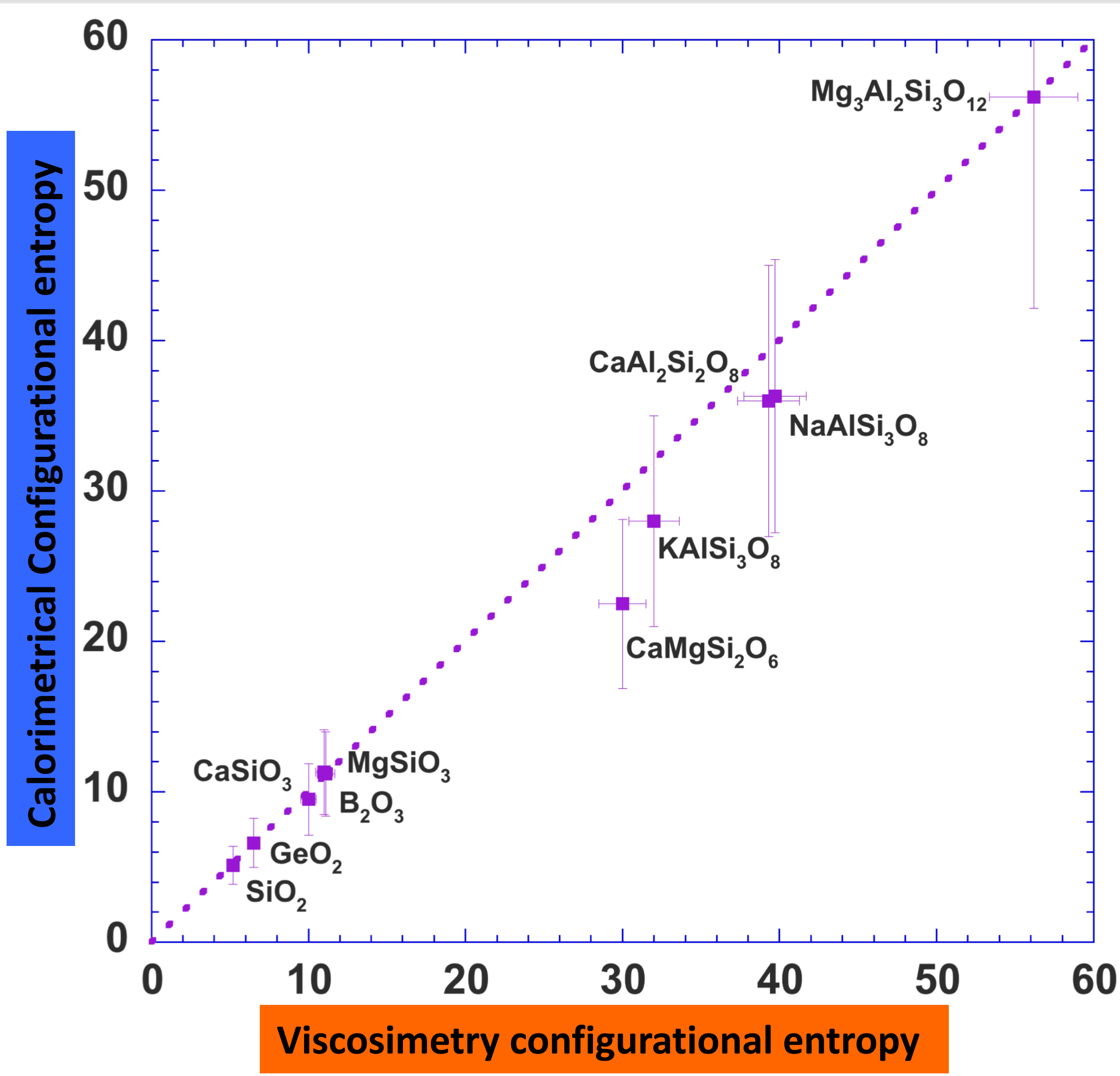
Proposed by Adam and Gibbs, 1964

First used to silicate melts by **Urbain, 1972, Scherer, 1984, Richet, 1984, Neuville and Richet, 1991….**

$$S^{conf}(T) = S^{conf}(Tg) + \int_{Tg}^{T} Cp^{conf} / T dt$$

$$Cp^{conf}(T) = Cpg(Tg) - Cpl(T)$$

Calorimetry measurements
=> Easy


Calorimetrical Configurational entropy
Viscosimetry configurational entropy
0
10
20
30
40
50
60
$Mg_3Al_2Si_3O_{12}$
$CaAl_2Si_2O_8$
$NaAlSi_3O_8$
$KAlSi_3O_8$
$CaMgSi_2O_6$
$CaSiO_3$
$MgSiO_3$
B_2O_3
GeO_2
SiO_2

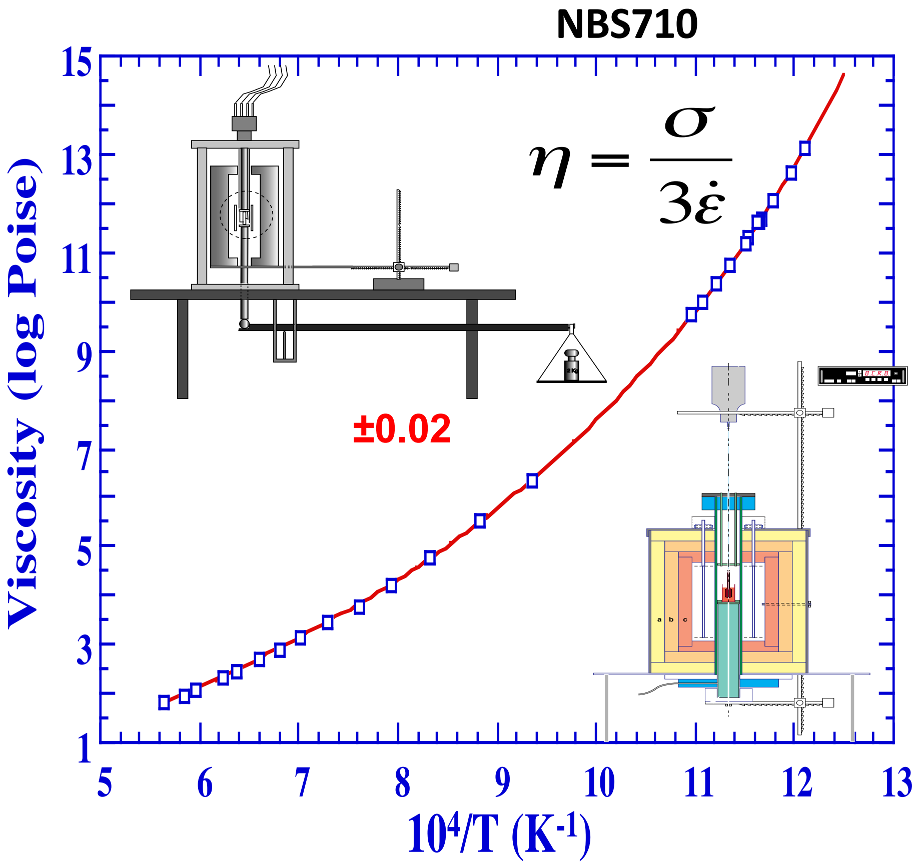
- Viscosity and configurational entropy

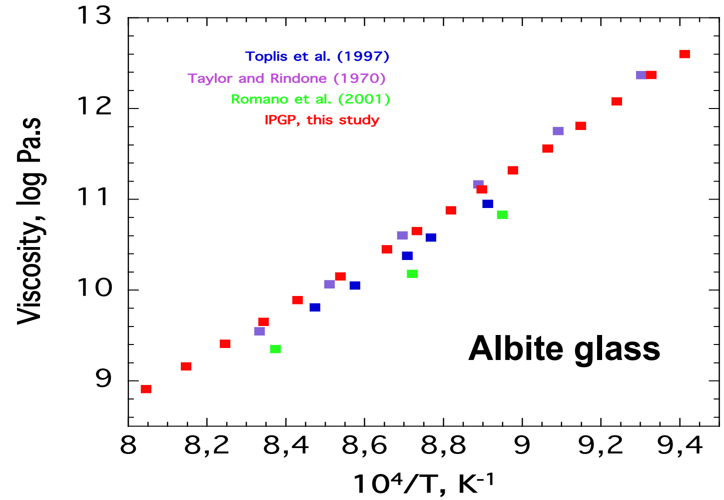
  Ca/Mg silicate, and Ca/Na silicate glasses

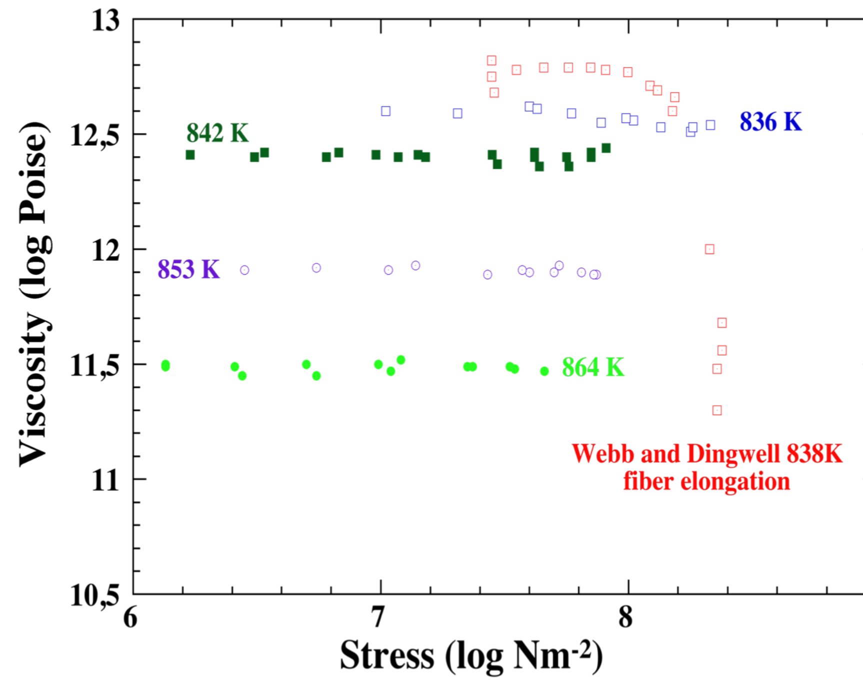
- Configurational entropy and glass structure

  Ca/Mg/Na in aluminosilicate glasses and melts

- Mix alkali effect? Na/K

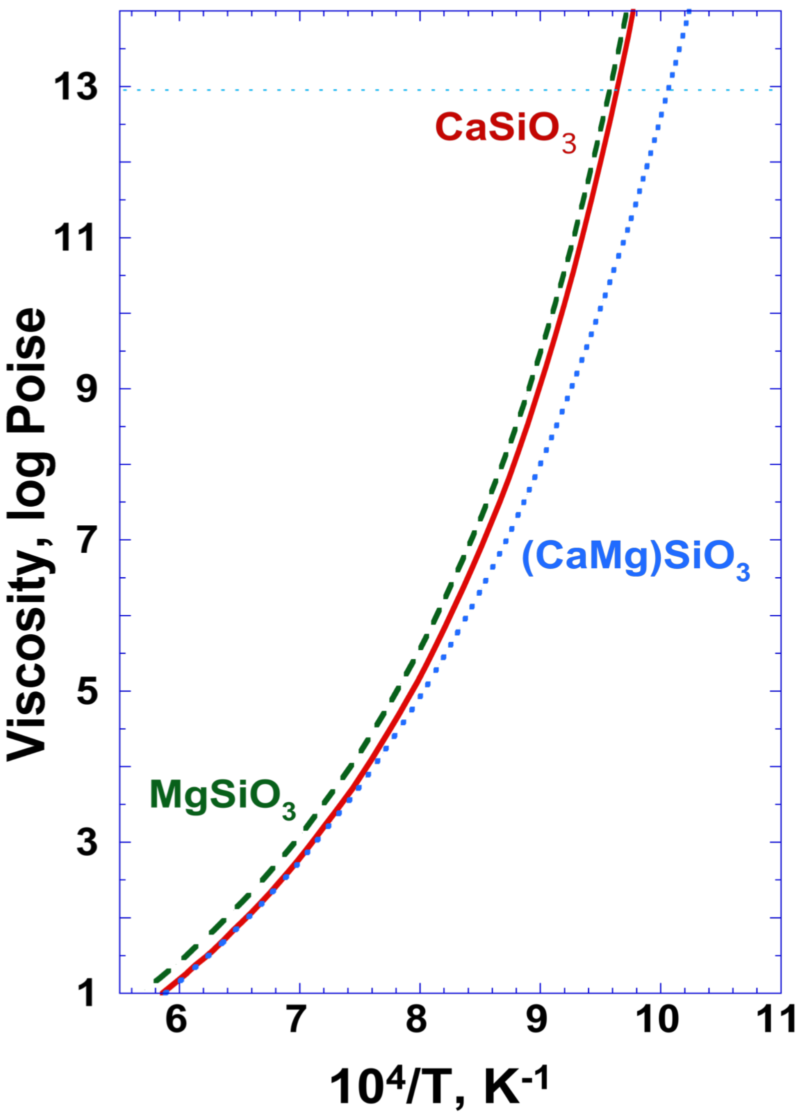


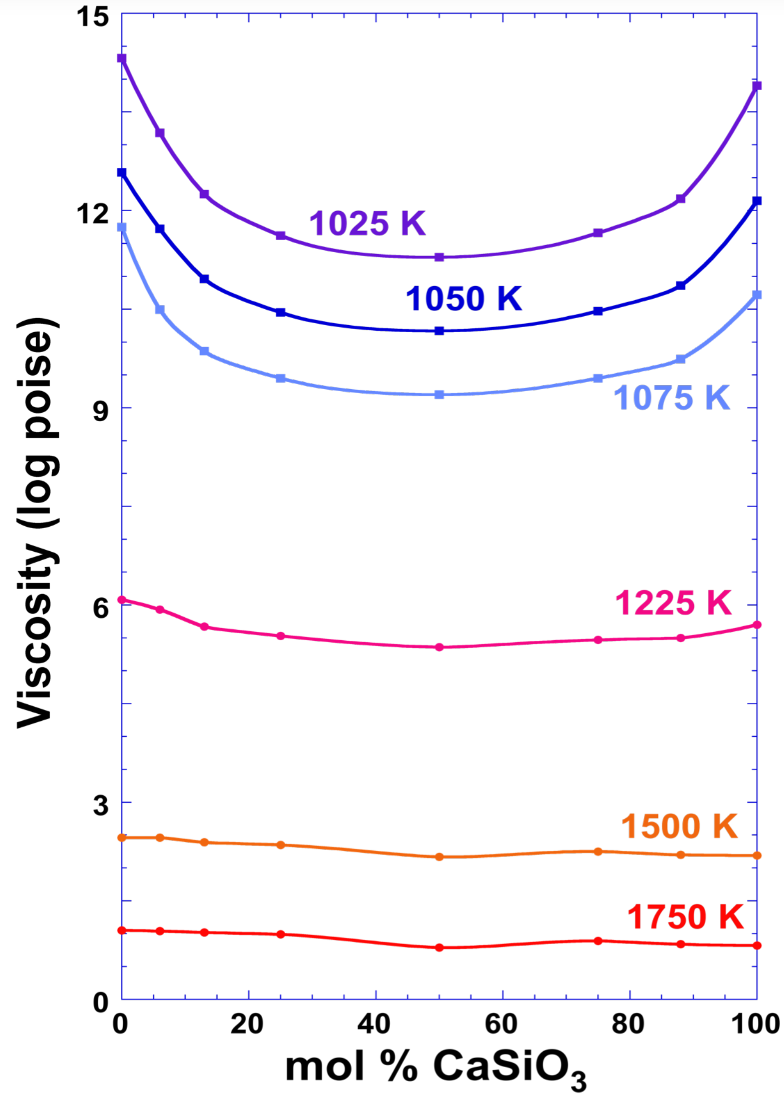




Neuville D.R. (2006) Viscosity, structure and mixing in (Ca, Na) silicate melts. Chem. Geol., 229, 28-42.

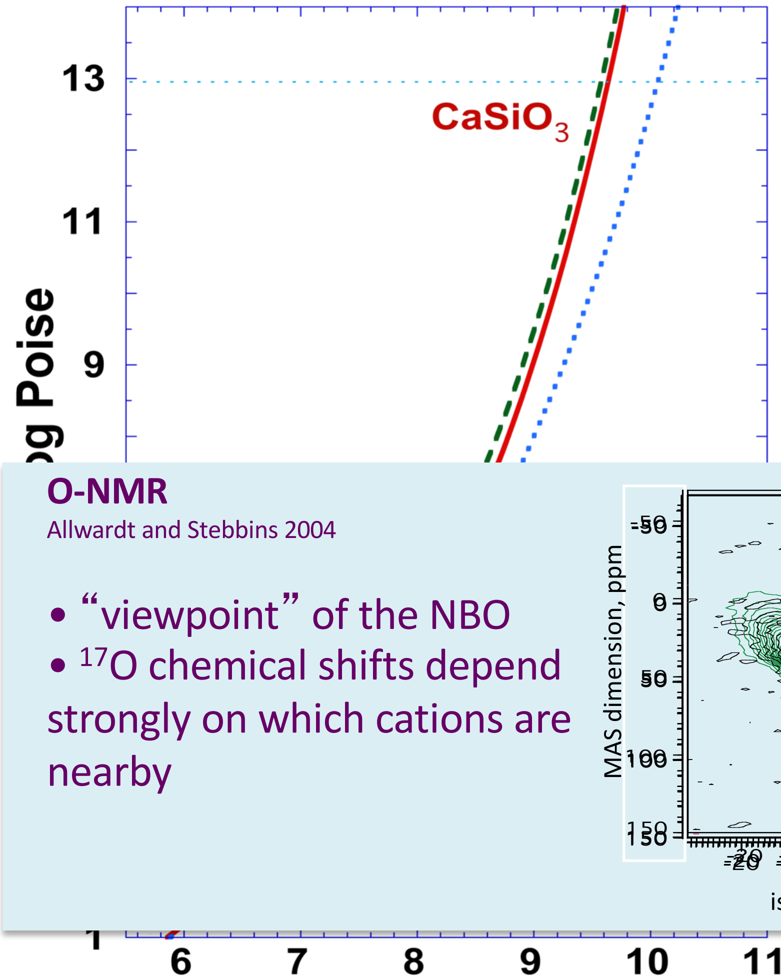
Ca/Mg Mixing ?

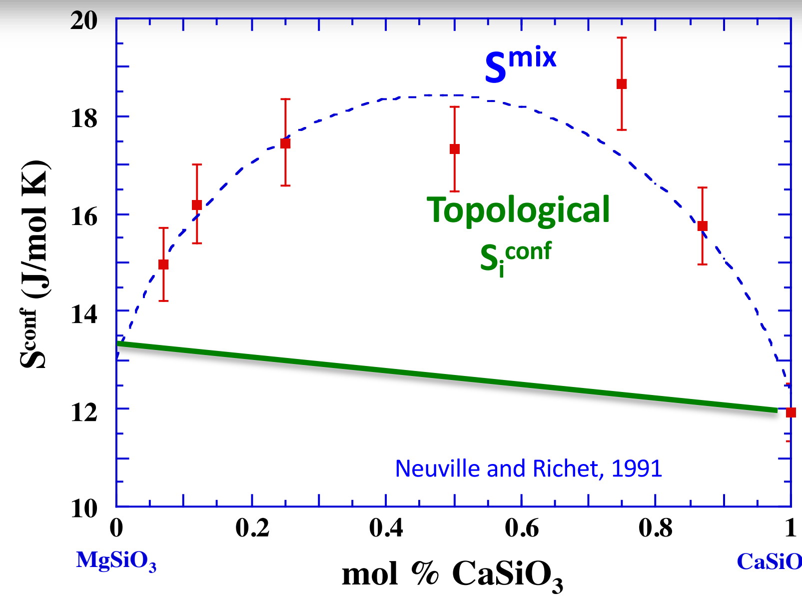




Neuville D.R. and Richet P. (1991) Viscosity and mixing in molten (Ca,Mg) pyroxenes and garnets. Geochim. Cosmochim. Acta., 55, 1011-1021.

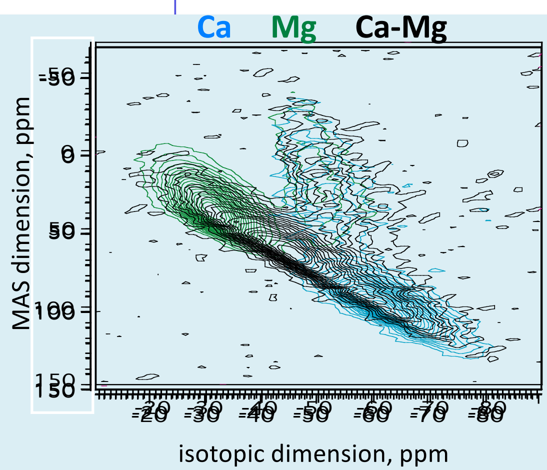
$$\log \eta = A_e + B_e/TS^{conf}(T)$$





O-NMR
Allwardt and Stebbins 2004

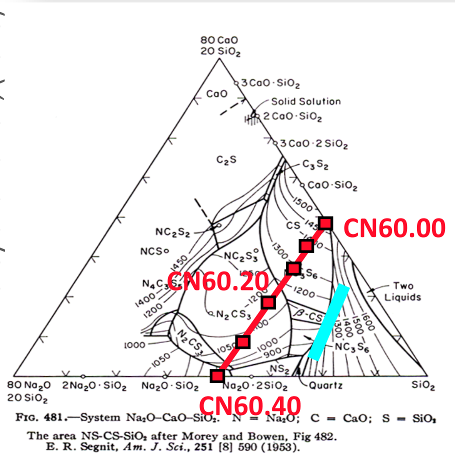
- "viewpoint" of the NBO
- ^{17}O chemical shifts depend strongly on which cations are nearby

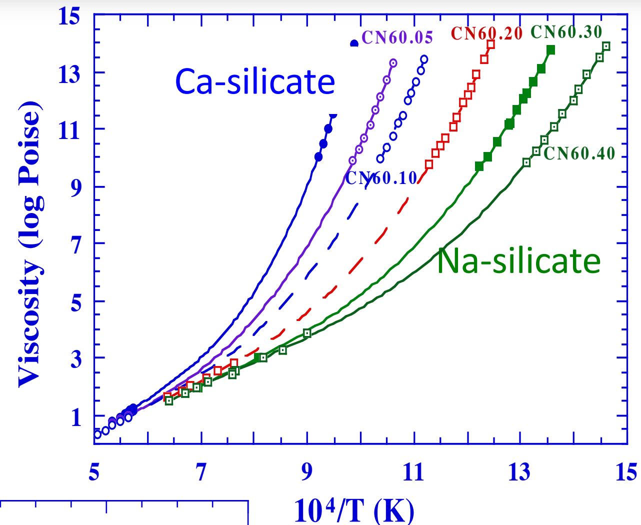


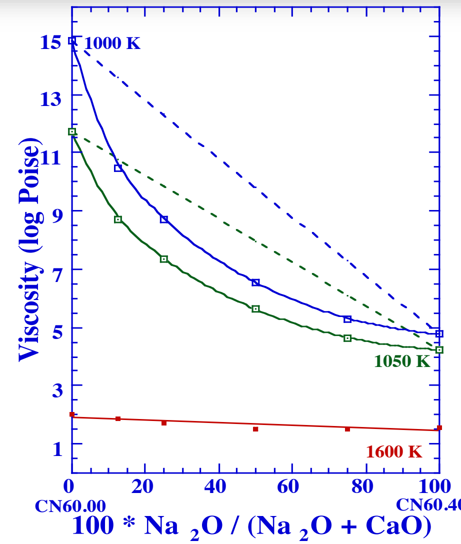
- **detailed analyses of spectra support almost random distribution of Ca + Mg around NBO**
- **size difference of Ca^{2+} and Mg^{2+} is insufficient to cause ordering**

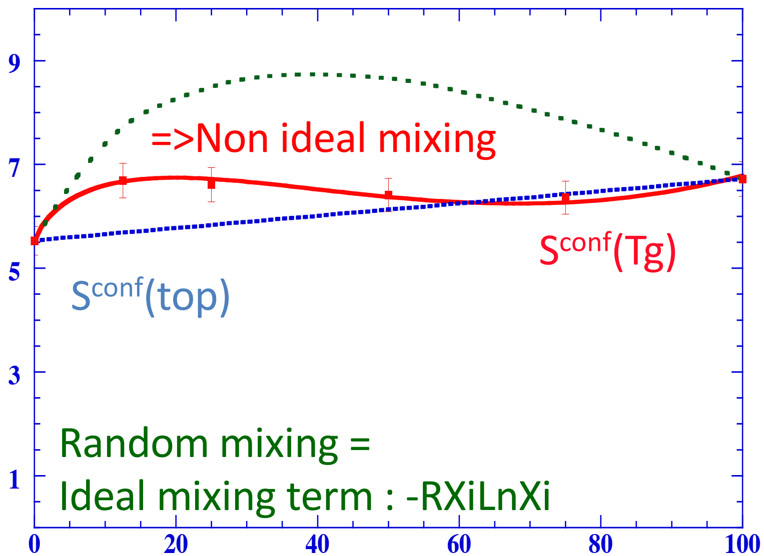
The configurational entropy: a "picture" of the network structure

Morey and Bowen, (1925)

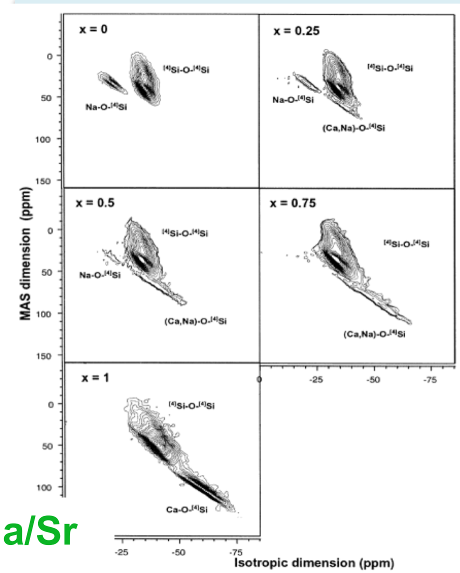








Ideal mixing does not work between Na/Ca and Na/Sr



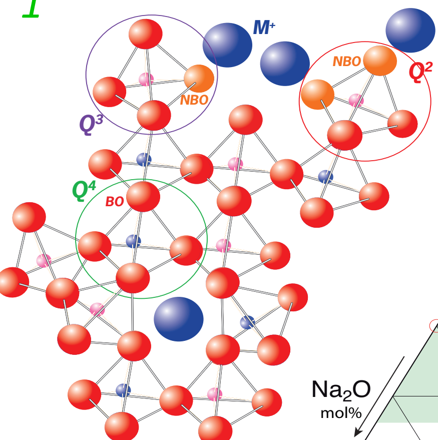
Raman spectrocopy (Neuville, 2006) and ^{17}O NMR (Lee and Stebbins, 2003) show a **non random distribution of Na and Ca.**

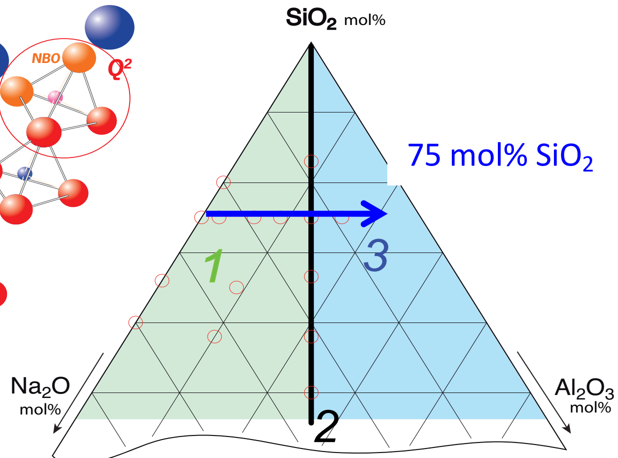
Neuville D.R., (2005) Structure,properties in (Sr, Na) silicate glasses and melts. Phys Chem Glasses, 46, 112-119
Neuville D.R. (2006) Viscosity, structure and mixing in (Ca, Na) silicate melts. Chem. Geol., 229, 28-42

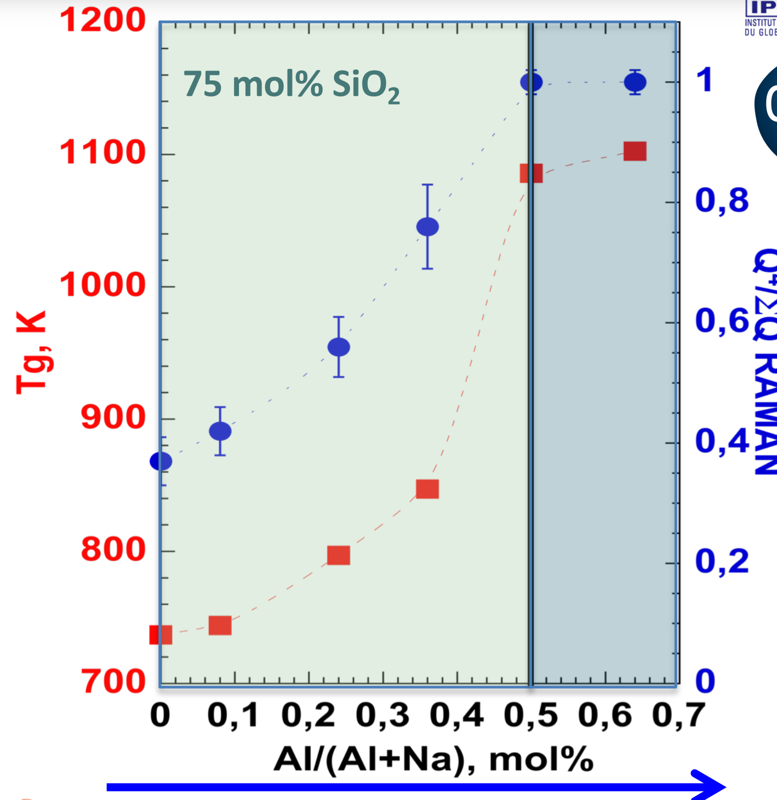
Summary Al effect

Na_2O substitution by Al_2O_3 :
⇒ Polymerization
⇒ Change Q^3 in Q^4
⇒ Al in Q^4 and Na charge compensator

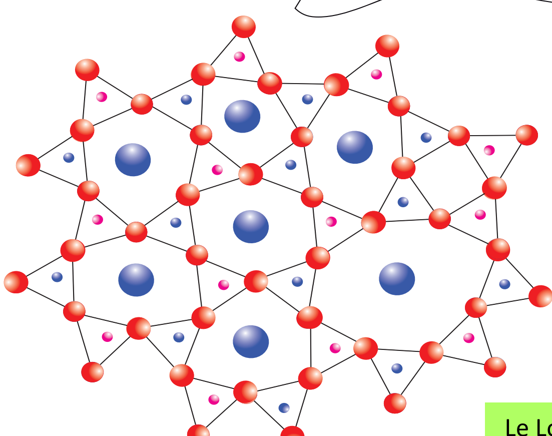
1

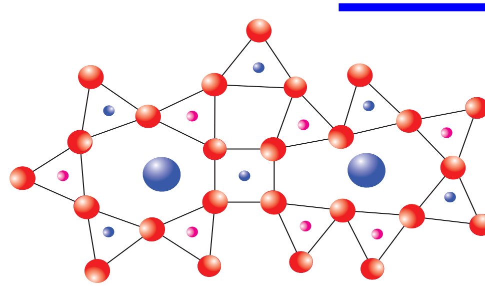






2

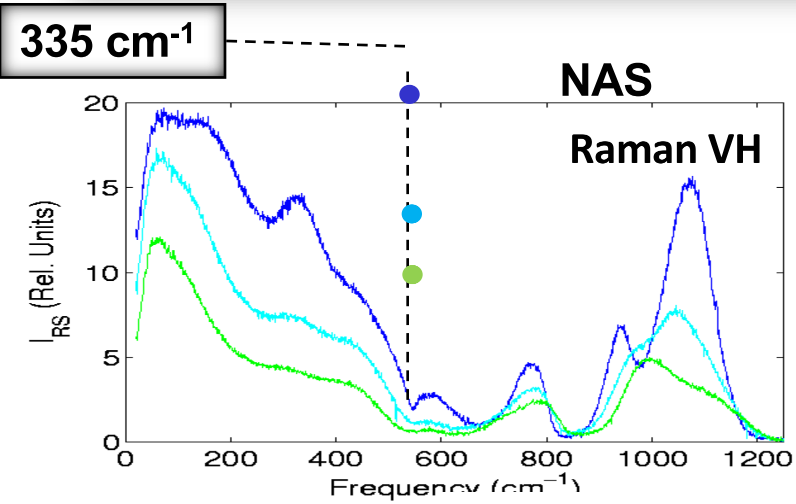




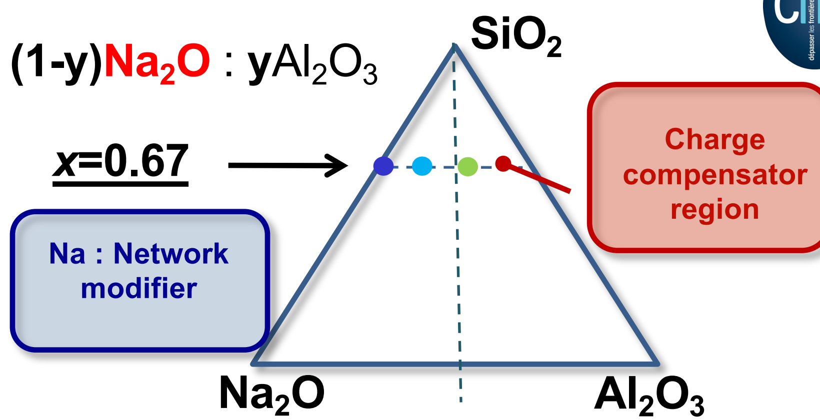
Al in CN 5 in peraluminous domain (*3*)

Le Losq Ch., Neuville D.R., Florian P., G.S. Henderson and Massiot D. (2014) Role of Al3+ on rheology and nano-structural changes of sodium silicate and aluminosilicate glasses and melts. Geochimica Cosmochimica Acta, 126, 495-517

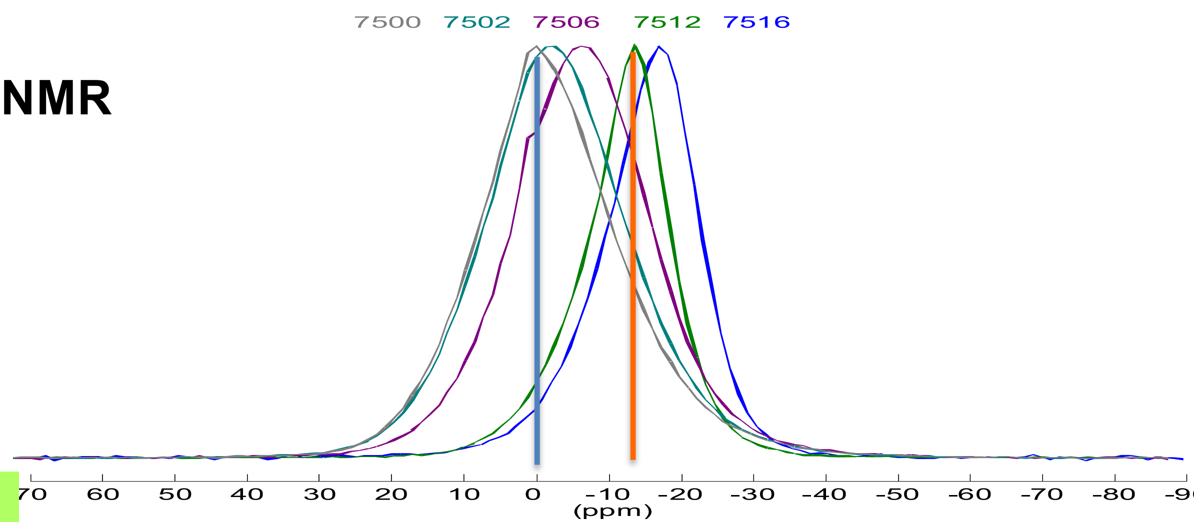
Hehlen B. and Neuville D.R. (2015) Raman response of network modifier cations in alumino-silicate glasses. The Journal of Physical Chemistry B. 119, 4093–4098.



xSiO$_2$: (1-y)Na$_2$O : yAl$_2$O$_3$



^{23}Na NMR



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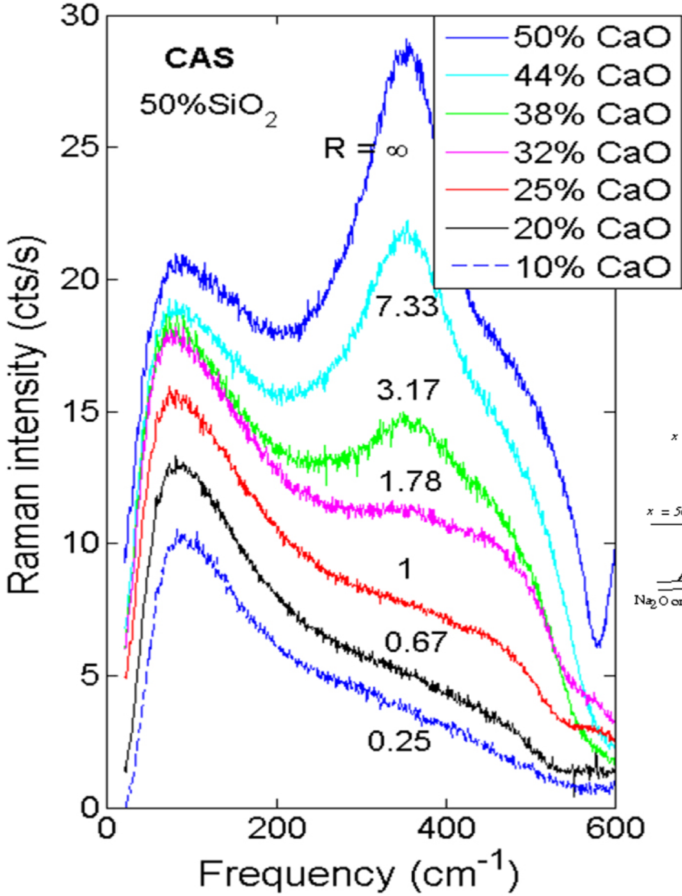
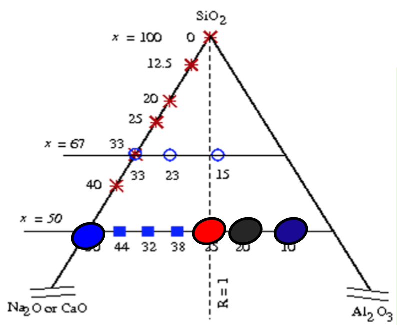
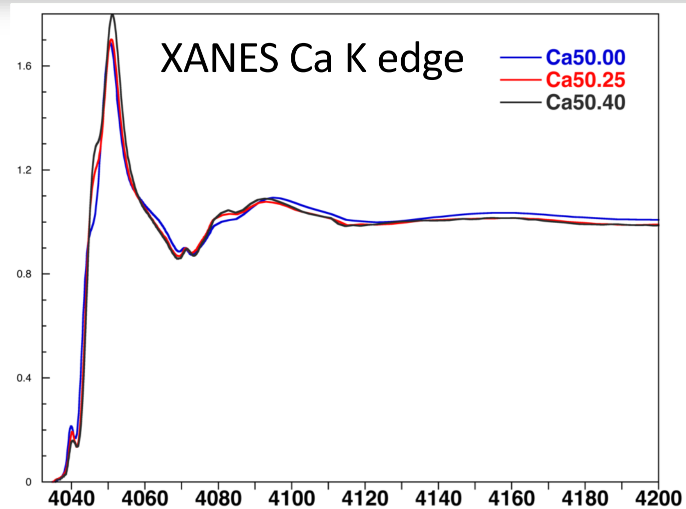
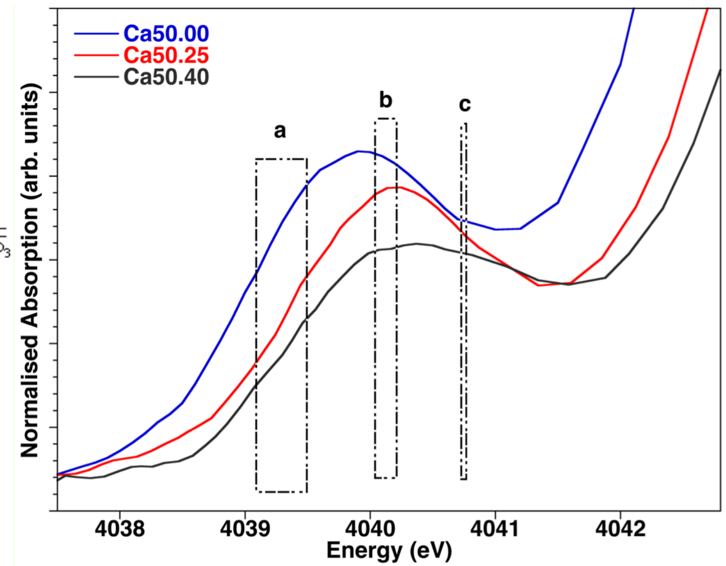
=> Important change in the Na Neighbors with Na/Al substitution

Raman VH





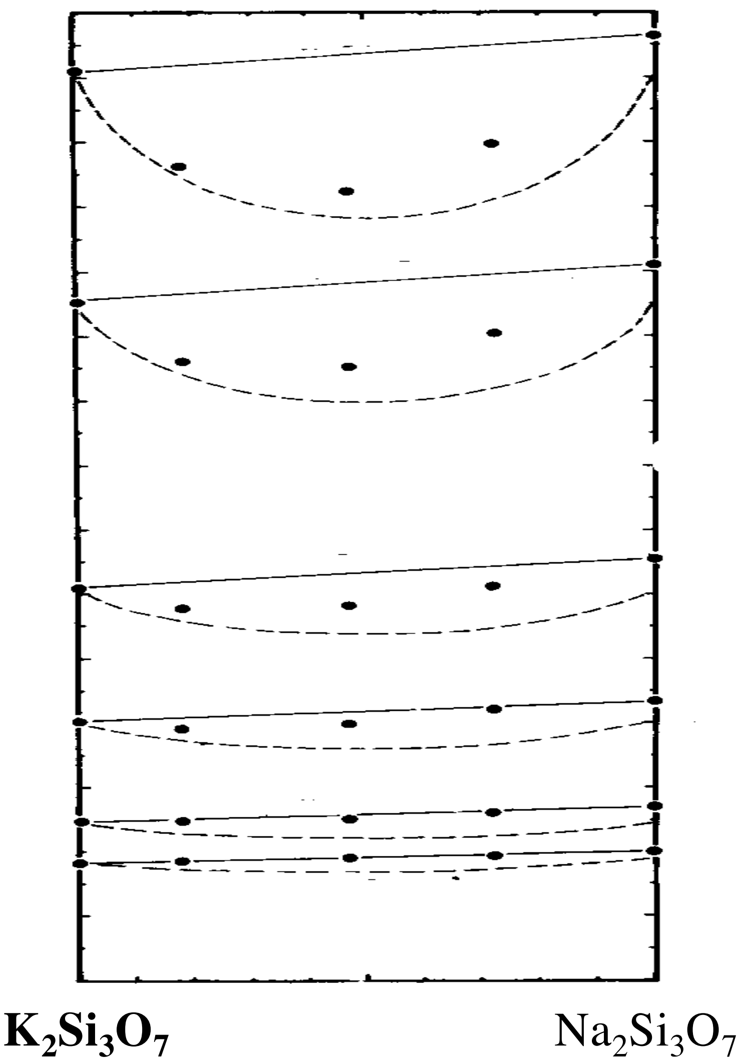




Hehlen B. and Neuville D.R. (2015) Raman response of network modifier cations in alumino-silicate glasses. The Journal of Physical Chemistry B. 119, 4093–4098.

Cicconi M.R., de Ligny D., Gallo T. M., Neuville D.R. (2016) Ca Neighbors from XANES spectroscopy: a tool to investigate structure, redox and nucleation processes in silicate glasses, melts and crystals. American Mineralogist, 101, 1232-1236.

The mixed alkali effect on the viscosity of silicate melts



$$\log(\eta) = A_e + \frac{B_e}{T \times S^{conf}(T)}$$

$$S^{conf}(T) = S^{conf}(Tg) + \int_{Tg}^{T} \frac{Cp^{conf}(T)}{T} dT$$

$$S^{conf}(Tg) = \sum x_i \times S^{conf}_{(i)} - nRx_i \ln(x_i)$$

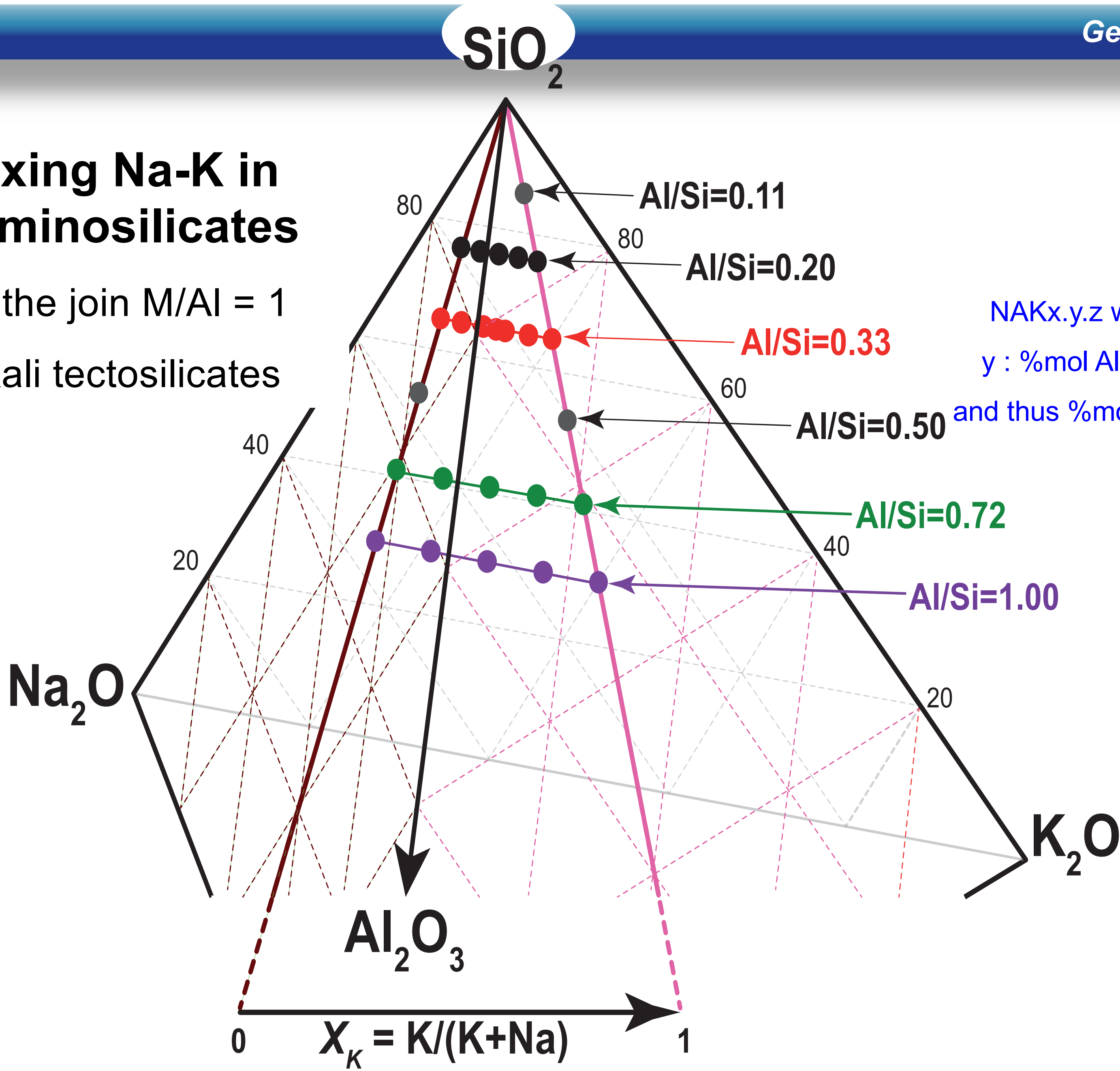
Random mixing of Na and K

Poole Data 1948, Model Richet (1984)

Mixing Na-K in aluminosilicates

On the join M/Al = 1

Alkali tectosilicates



NAKx.y.z with x : %mol SiO_2 ;

y : %mol Al_2O_3 ; z : %mol K_2O ;

and thus %mol Na_2O = 100-(x+y+z)

Al/Si=0.11 =90%SiO_2

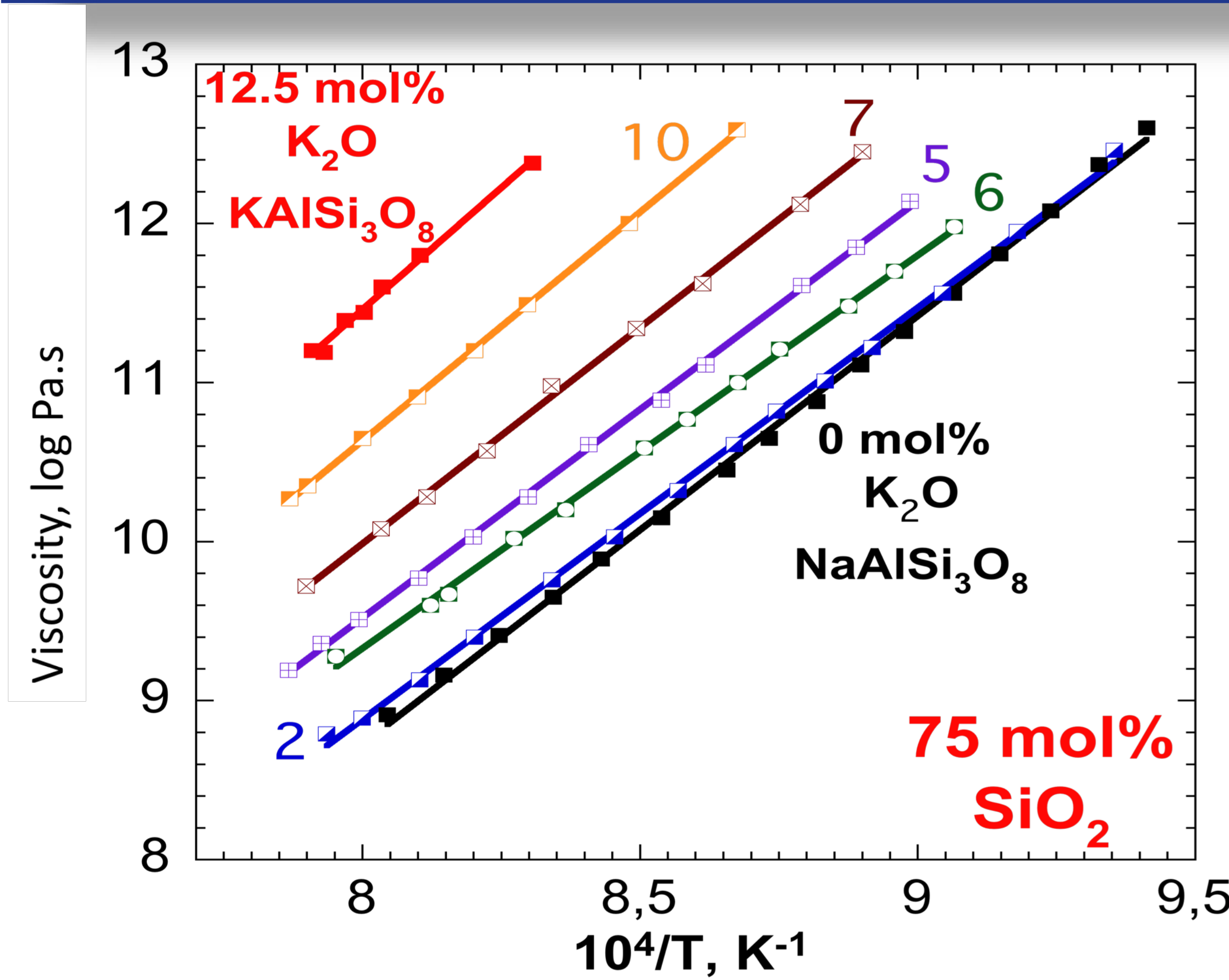
Al/Si=0.20 =83%SiO_2

Al/Si=0.33 =75%SiO_2

Al/Si=0.50 =66%SiO_2

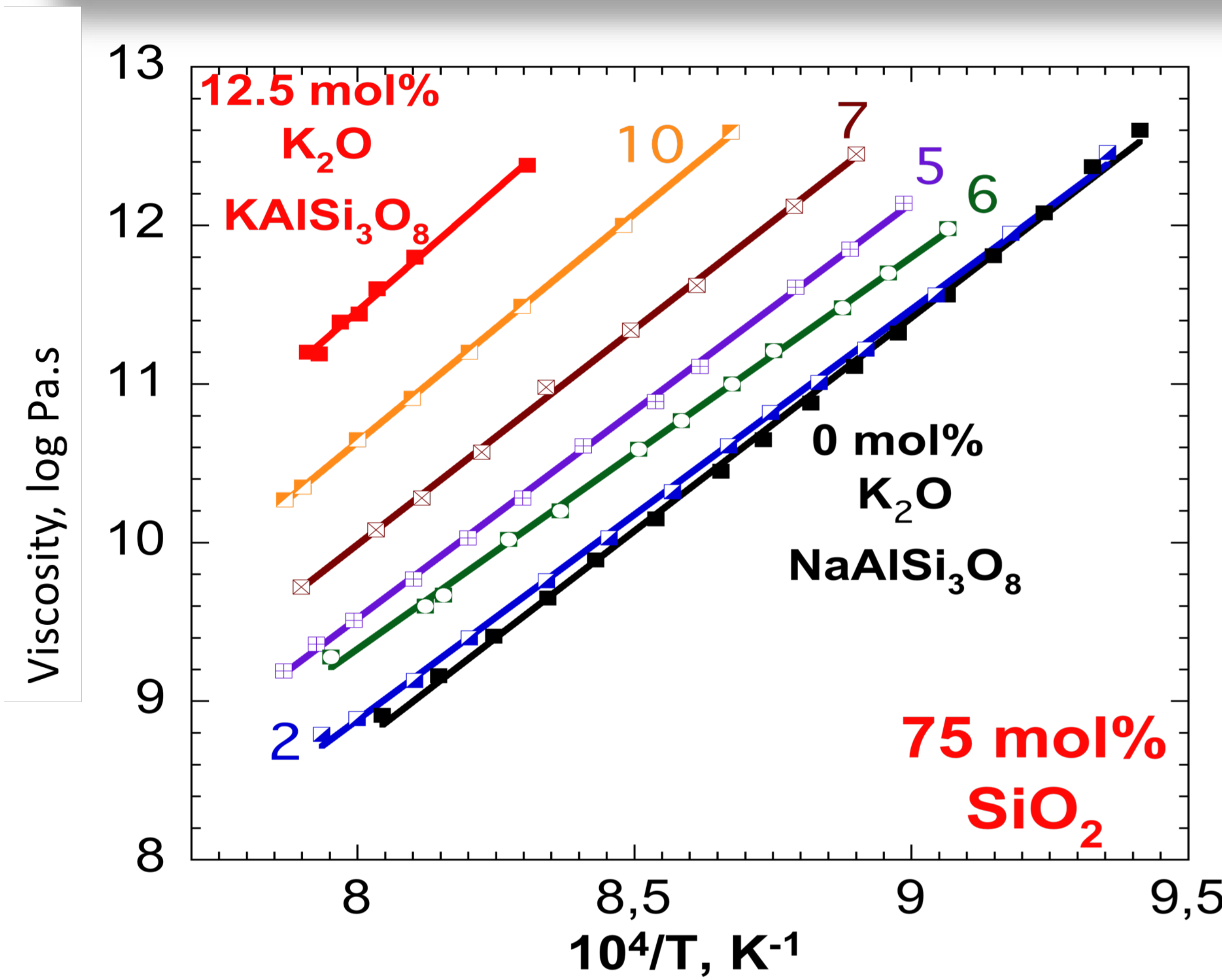
Al/Si=0.72 =58%SiO_2

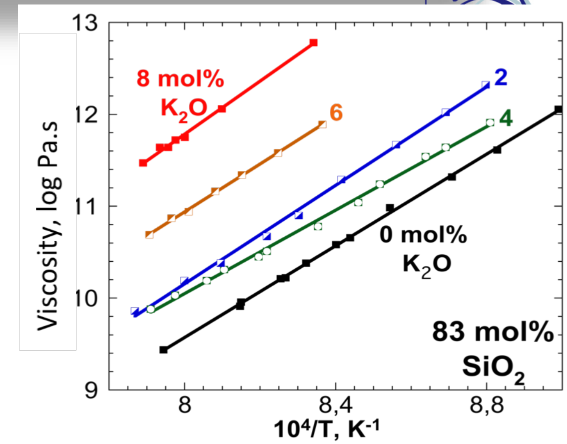
Al/Si=1.00 =50%SiO_2

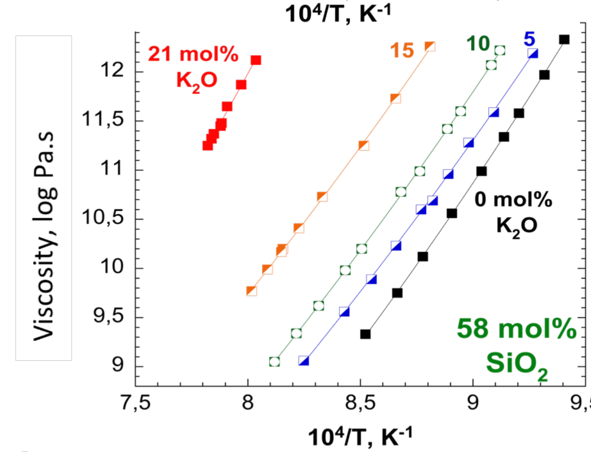


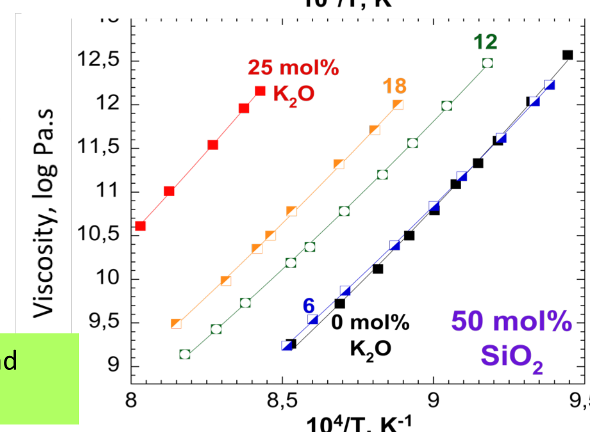
When replacing Na by K: viscosity increases strongly…

Losq C. and Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. Chemical Geology, 346, 57-71.









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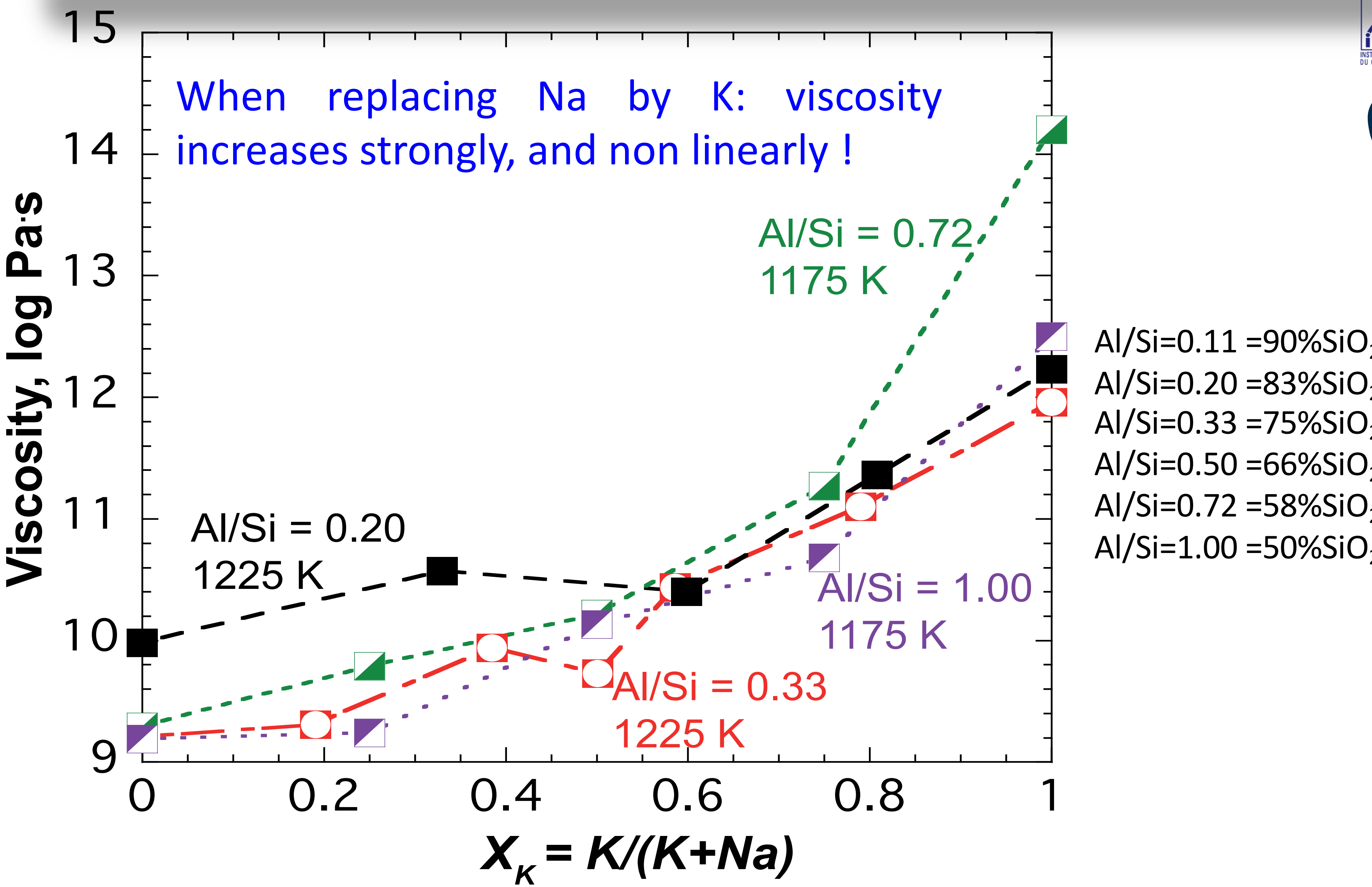
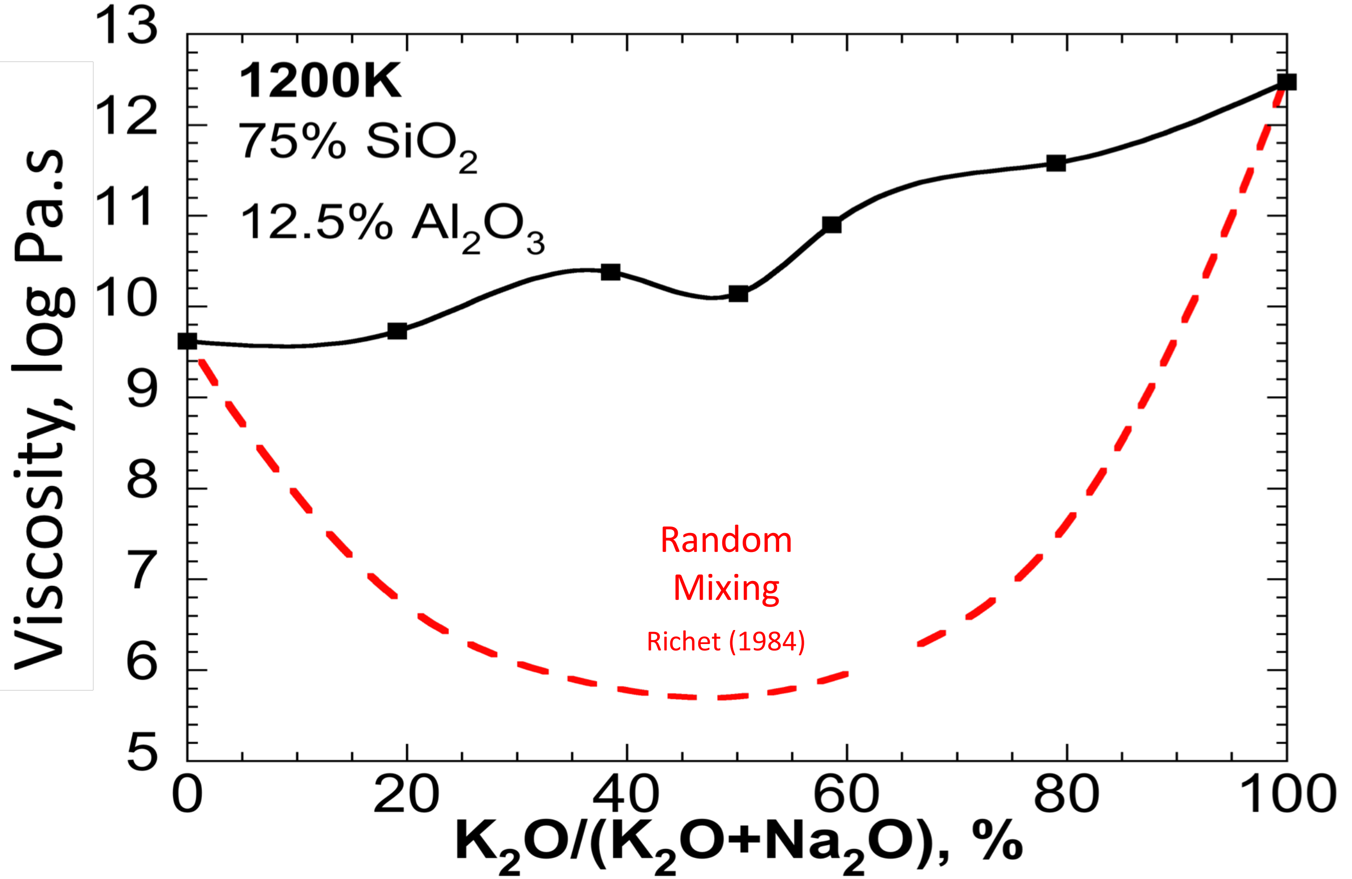


Le Losq C, Neuville D.R., Florian P., Massiot D., Zhou Z., Chen W., Greaves N. (2017) Percolation channels: a universal idea to describe the atomic structure of glasses and melts. Scientific Reports, 7, Article number: 16490, doi:10.1038/s41598-017-16741-3

Mixed albite-orthoclase melts $NaAlSi_3O_8$-$KAlSi_3O_8$

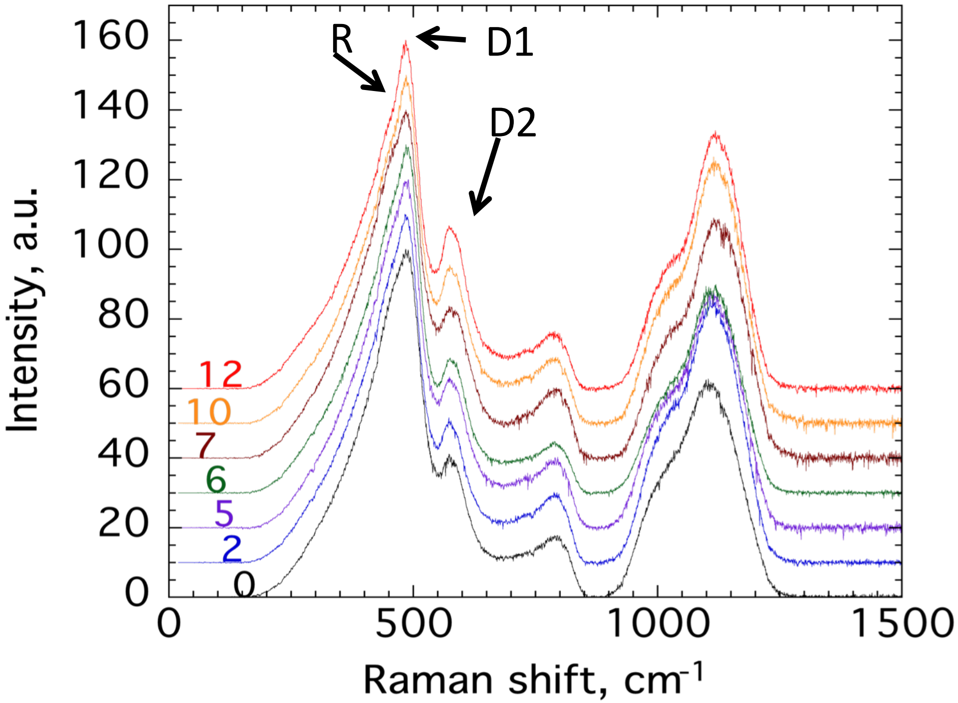


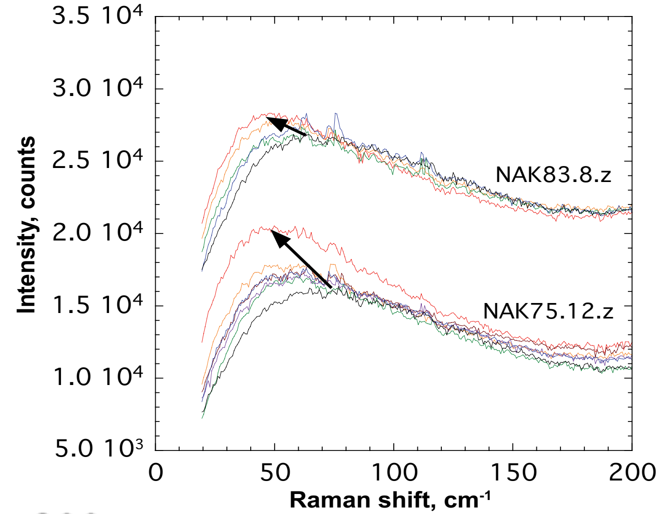
Na and K do not mix randomly

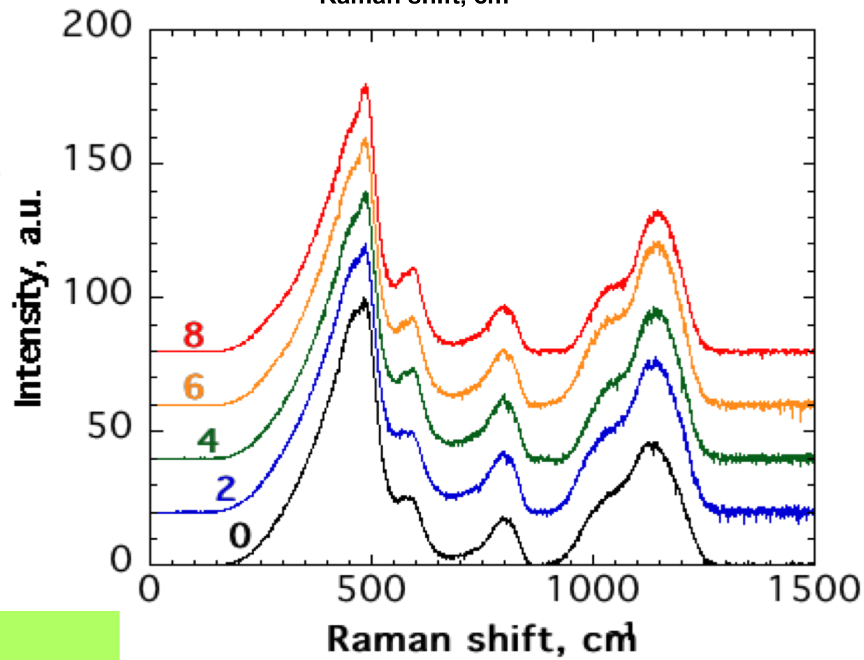
⇒ Viscosity, thermodynamics

⇒ Structure

Losq C. and Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. Chemical Geology, 346, 57-71.

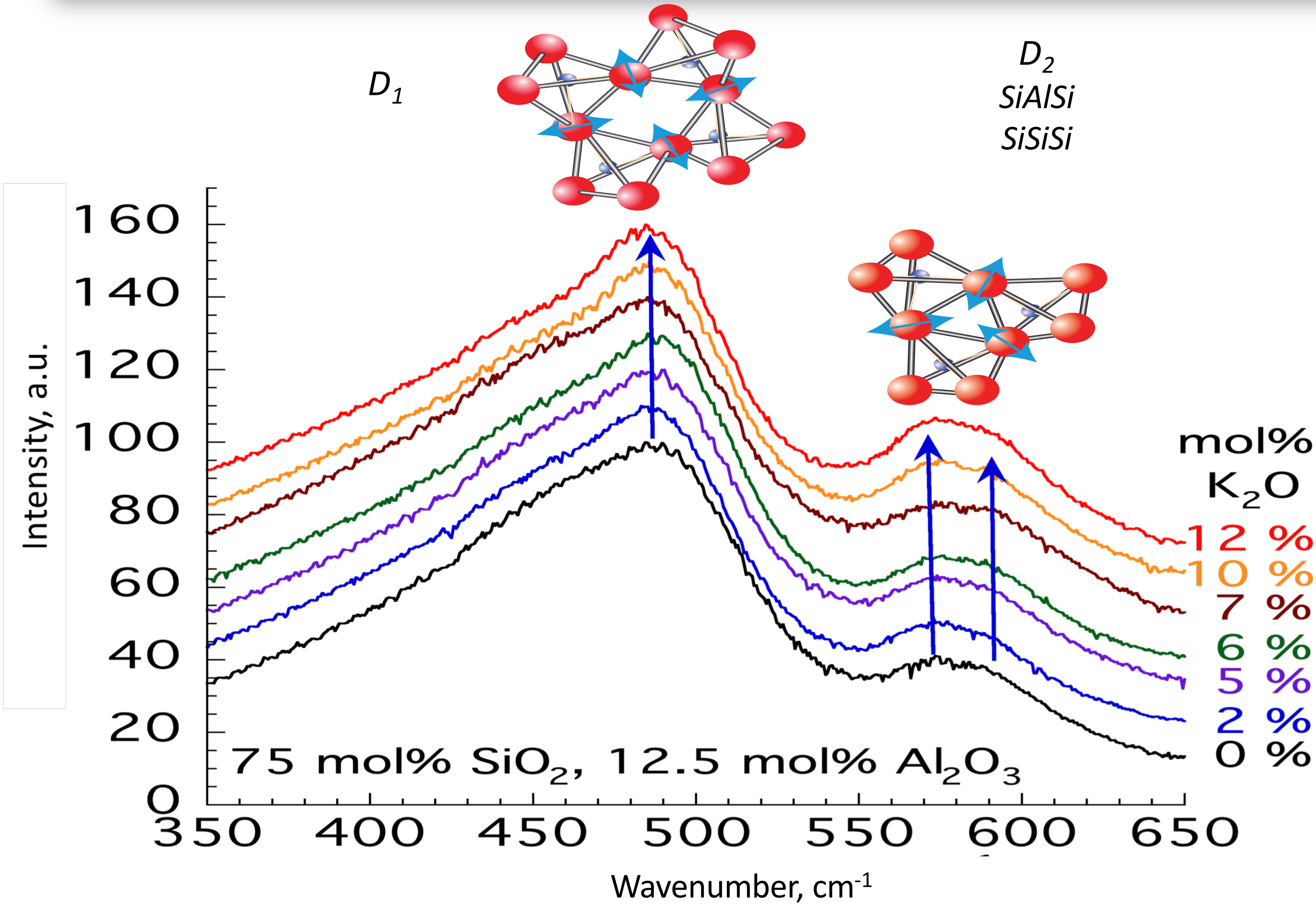






- Boson peak increase in I and decreases in frequency with K like close than SiO2
- D1 and D2 increase with K
- New D2 band

Losq C. and Neuville D.R. (2013) Effect of K/Na mixing on the structure and rheology of tectosilicate silica-rich melts. Chemical Geology, 346, 57-71.



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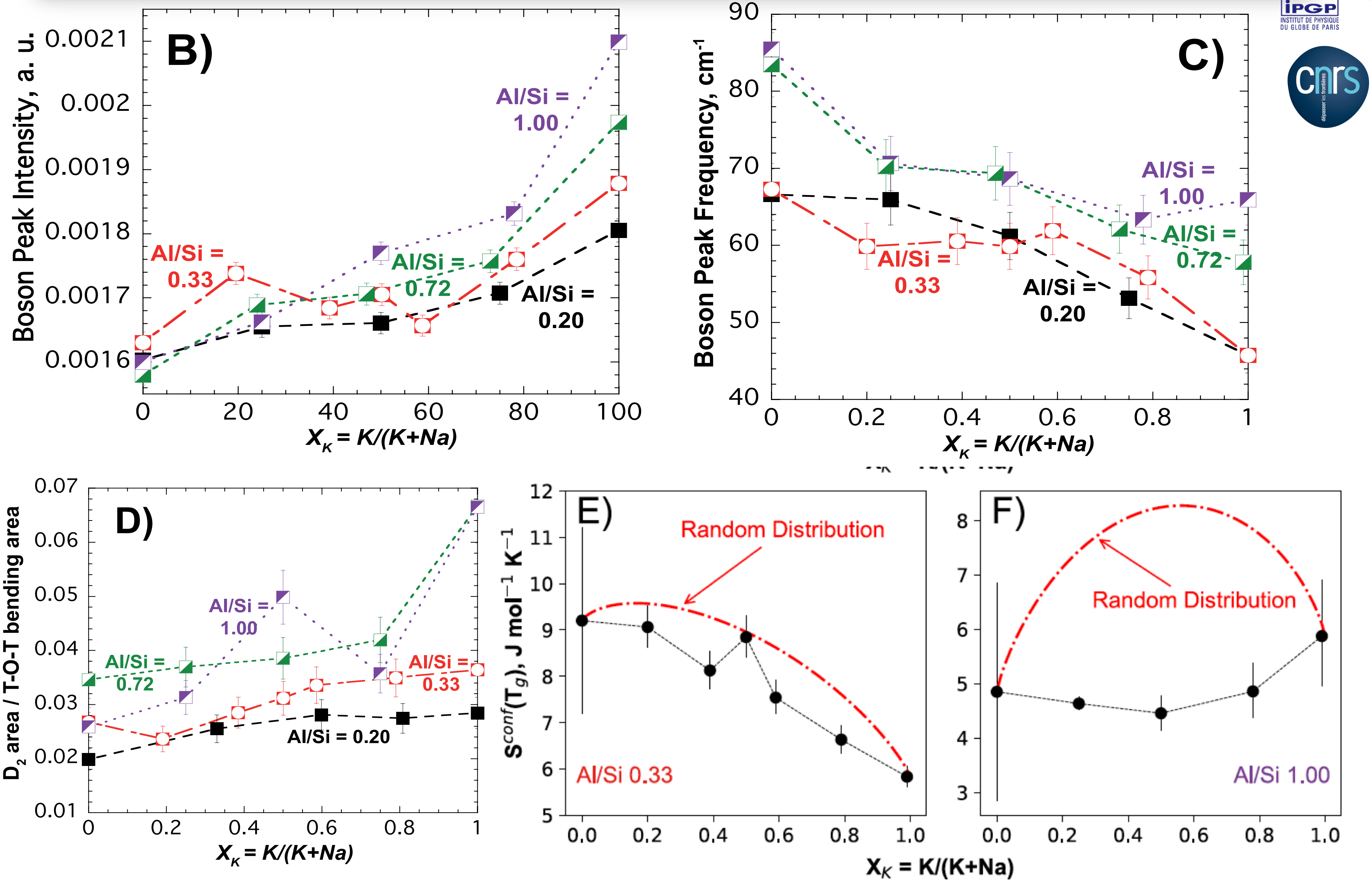
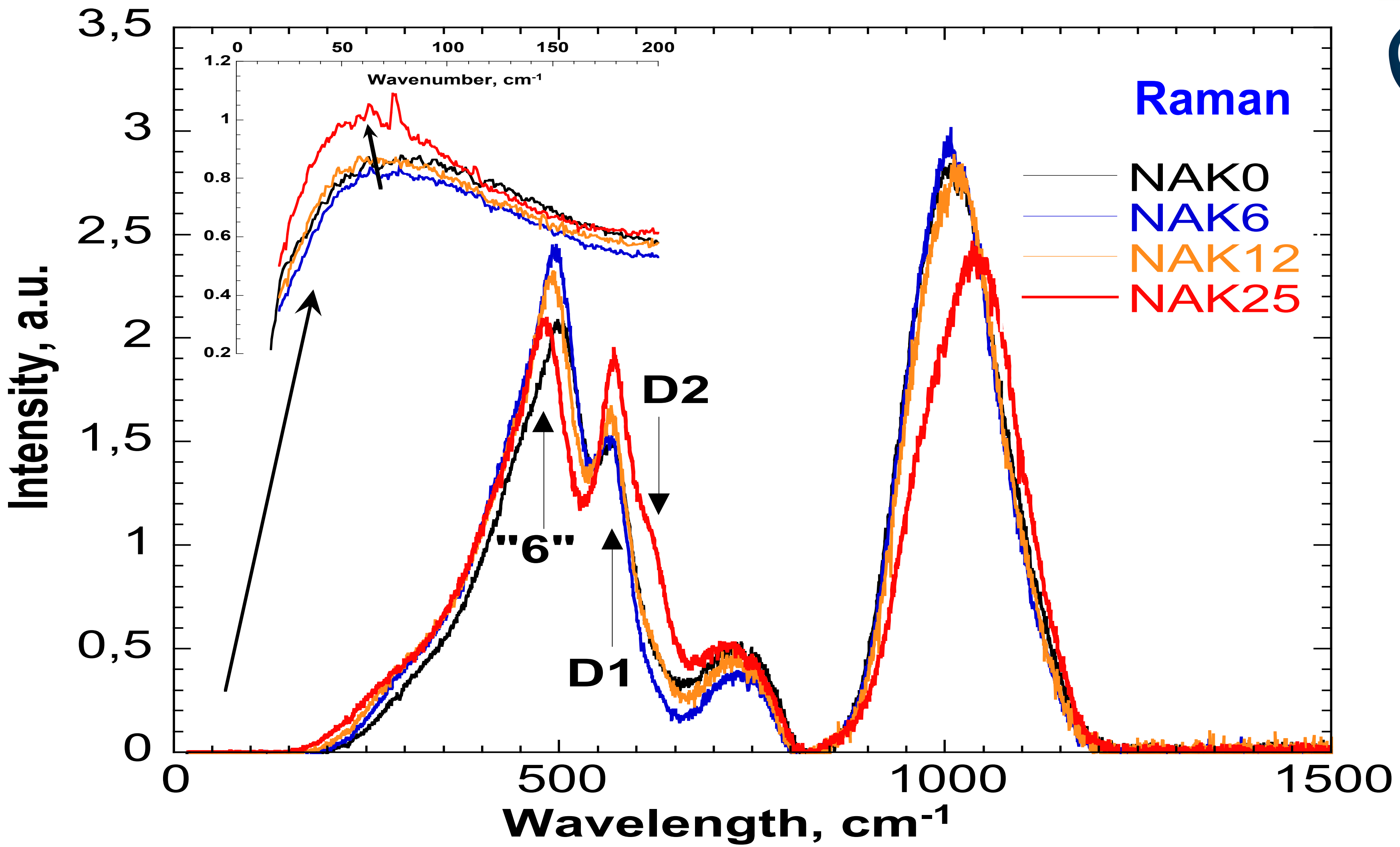

B)
Boson Peak Intensity, a. u.
0.0021
0.002
0.0019
0.0018
0.0017
0.0016
Al/Si = 1.00
Al/Si = 0.33
Al/Si = 0.72
Al/Si = 0.20
0
20
40
60
80
100
X_K = K/(K+Na)
C)
Boson Peak Frequency, cm-1
90
80
70
60
50
40
Al/Si = 1.00
Al/Si = 0.72
Al/Si = 0.33
Al/Si = 0.20
0
0.2
0.4
0.6
0.8
1
X_K = K/(K+Na)
D)
D2 area / T-O-T bending area
0.07
0.06
0.05
0.04
0.03
0.02
0.01
Al/Si = 1.00
Al/Si = 0.72
Al/Si = 0.33
Al/Si = 0.20
0
0.2
0.4
0.6
0.8
1
X_K = K/(K+Na)
E)
S^conf(Tg), J mol−1 K−1
12
11
10
9
8
7
6
5
Random Distribution
Al/Si 0.33
0.0
0.2
0.4
0.6
0.8
1.0
F)
8
7
6
5
4
3
Random Distribution
Al/Si 1.00
0.0
0.2
0.4
0.6
0.8
1.0
X_K = K/(K+Na)

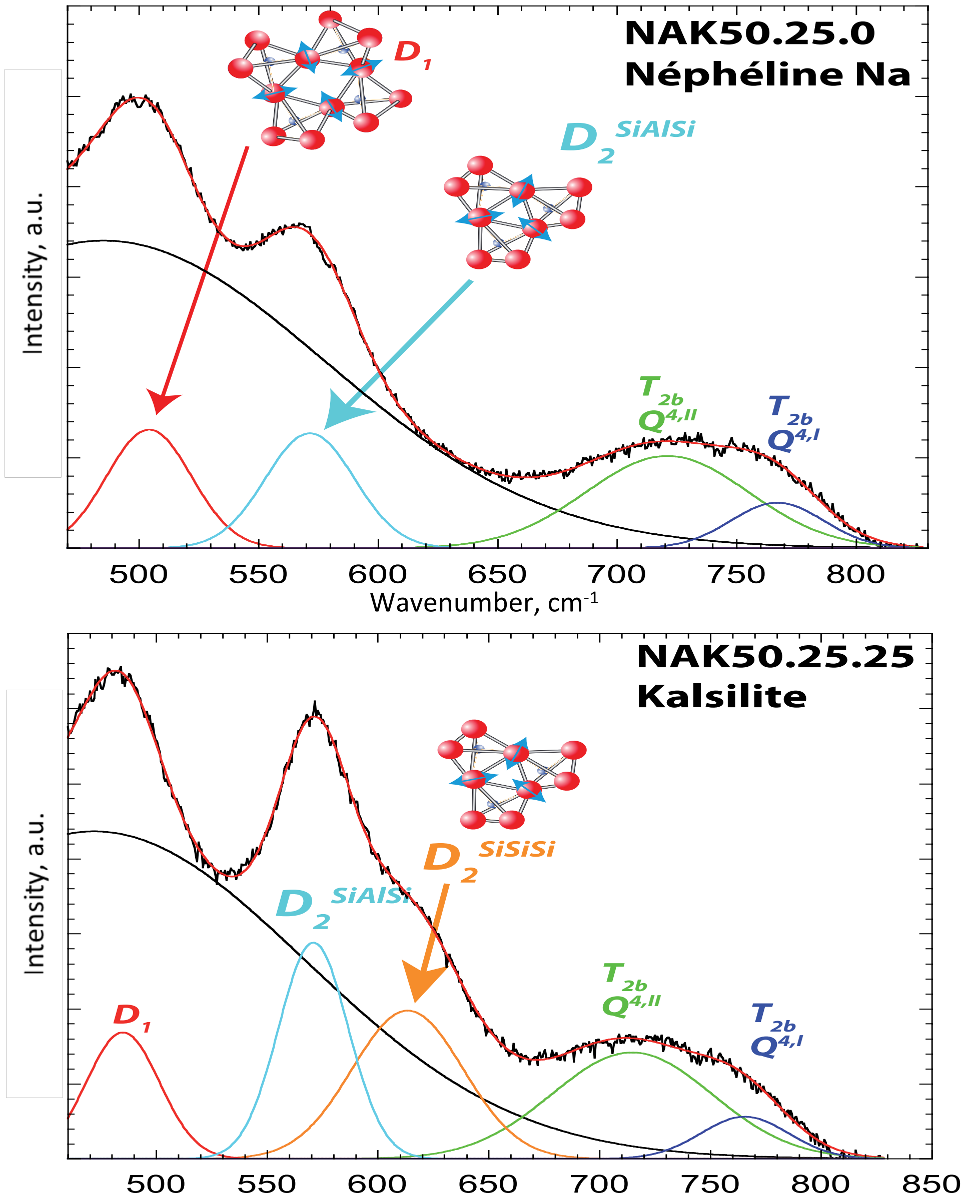


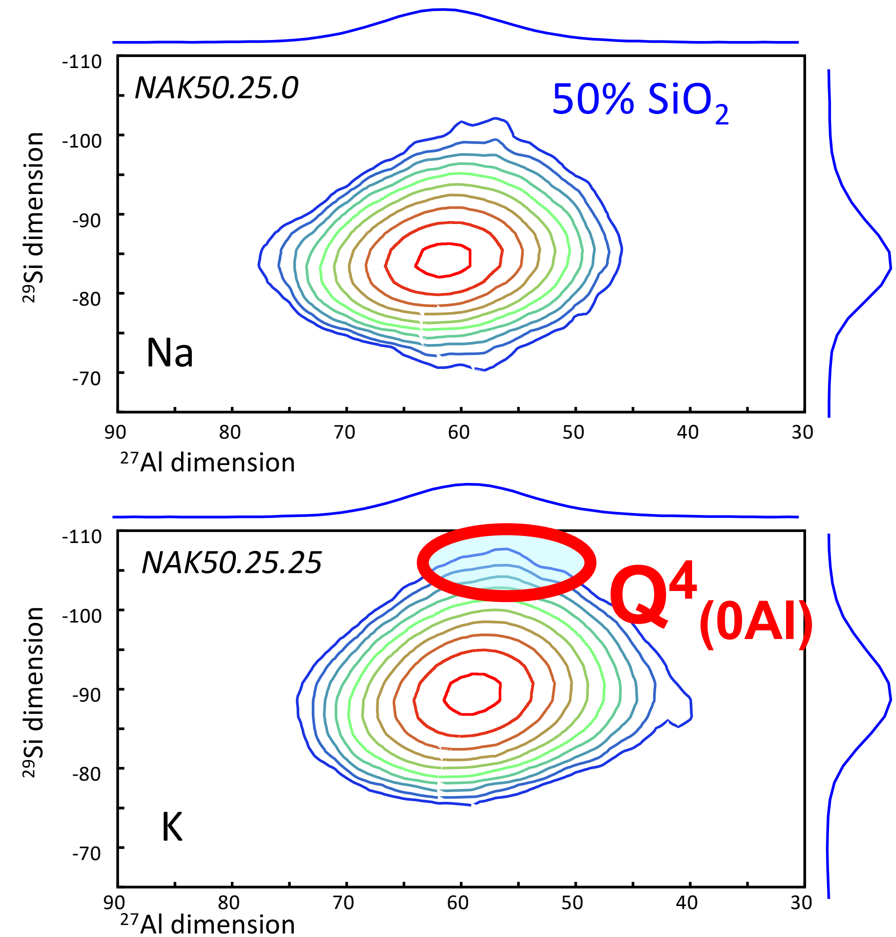
Le Losq C, Neuville D.R., Florian P., Massiot D., Zhou Z., Chen W., Greaves N. (2017) Percolation channels: a universal idea to describe the atomic structure of glasses and melts. Scientific Reports, 7, Article number: 16490, doi:10.1038/s41598-017-16741-3

At lower SiO_2 concentration…

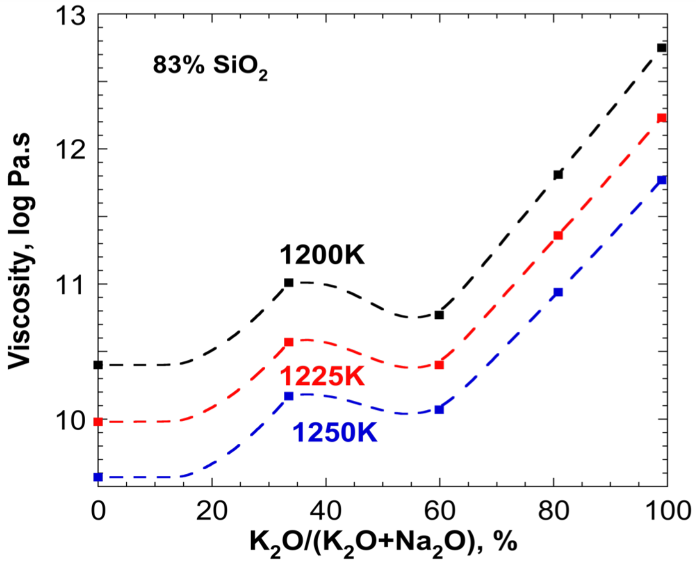
Glassy nepheline-kalsilite $NaAlSiO_4$-$KAlSiO_4$

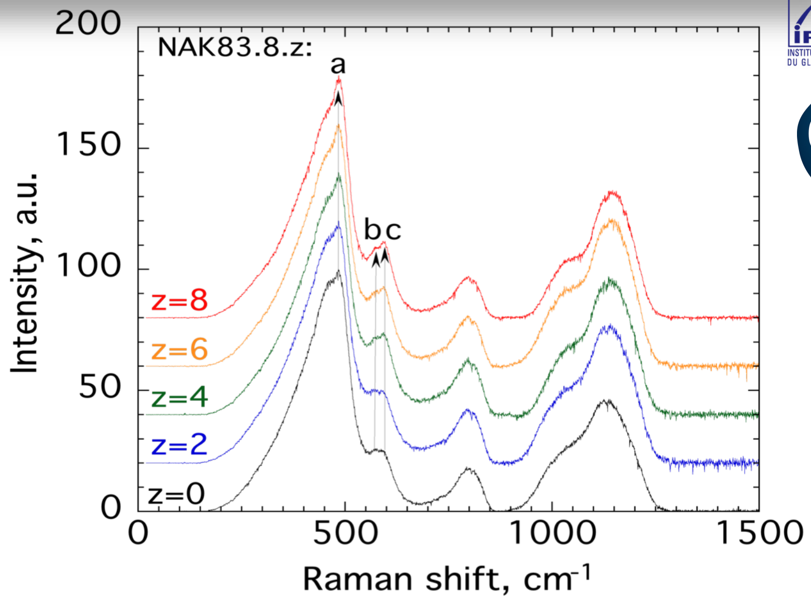
{29Si}27Al HMQC dipolar SR421 MAS 10kHz



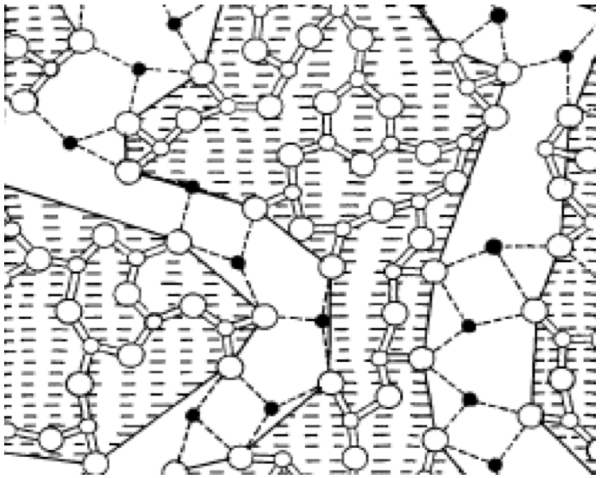


Le Losq C, Neuville D.R., Florian P., Massiot D., Zhou Z., Chen W., Greaves N. (2017) Percolation channels: a universal idea to describe the atomic structure of glasses and melts. Scientific Reports, 7, Article number: 16490, doi:10.1038/s41598-017-16741-3

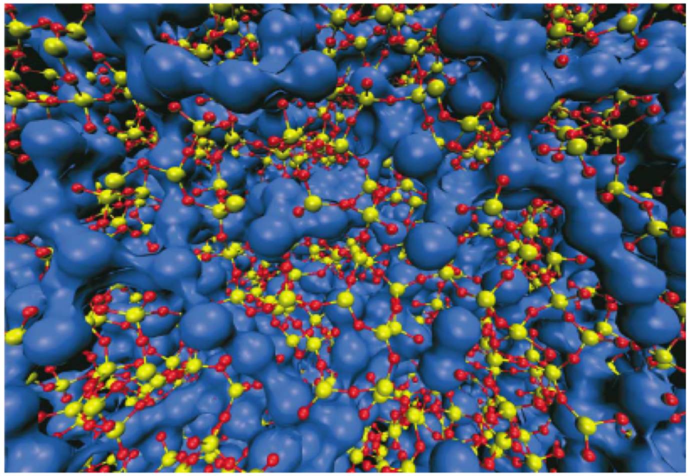




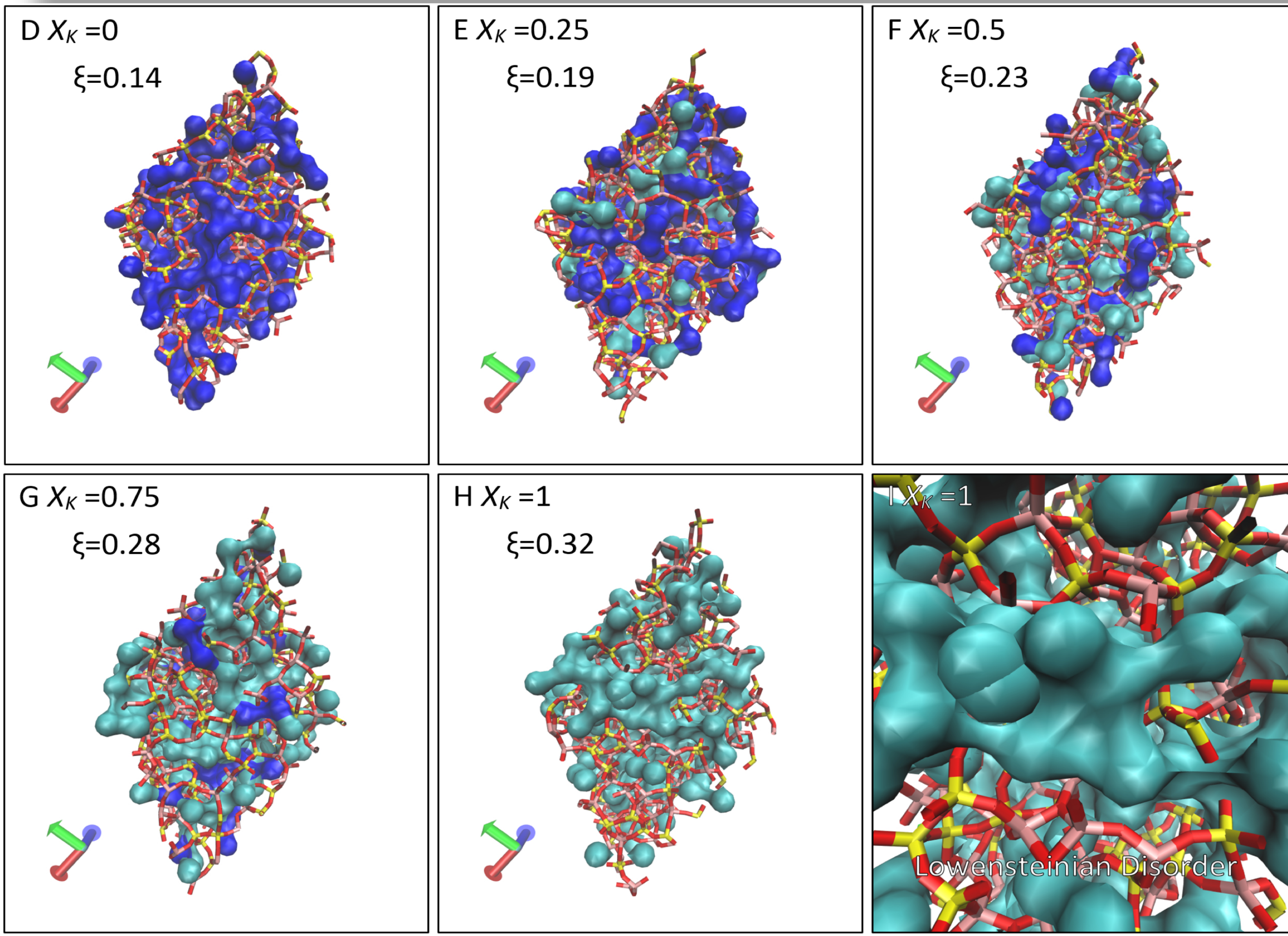
Greaves et al., 1981: MRN



Meyer et al., 2004



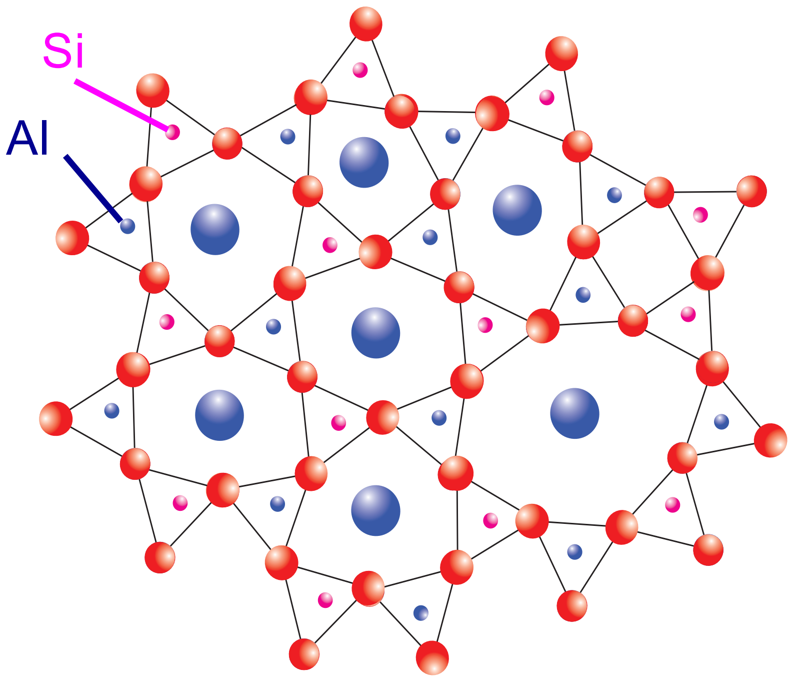
Le Losq C, Neuville D.R., Florian P., Massiot D., Zhou Z., Chen W., Greaves N. (2017) Percolation channels: a universal idea to describe the atomic structure of glasses and melts. Scientific Reports, 7, Article number: 16490, doi:10.1038/s41598-017-16741-3



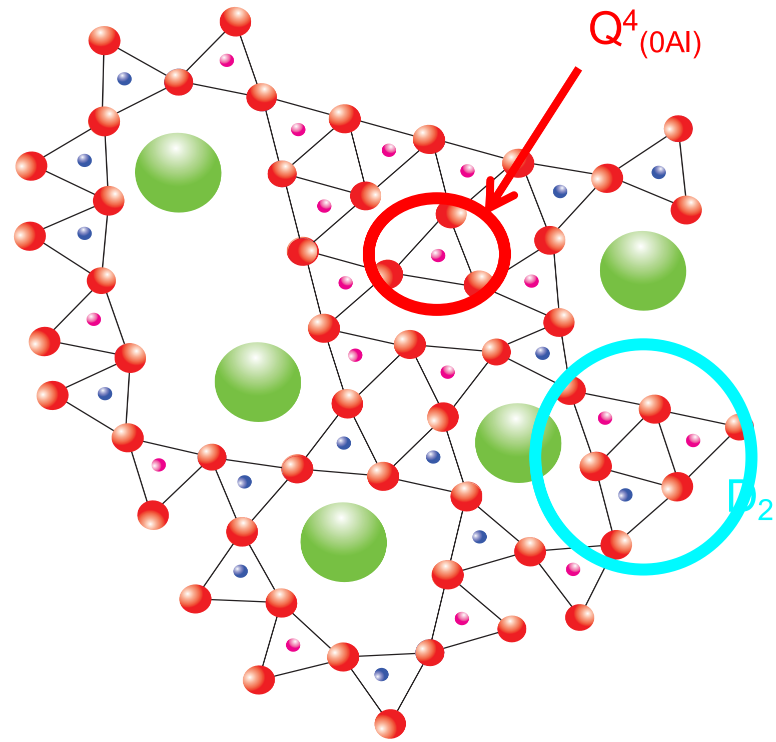
Le Losq C, Neuville D.R., Florian P., Massiot D., Zhou Z., Chen W., Greaves N. (2017) Percolation channels: a universal idea to describe the atomic structure of glasses and melts. Scientific Reports, 7, Article number: 16490, doi:10.1038/s41598-017-16741-3

Na tectosilicates K tectosilicates

Geomaterial



Compensated Continuous
Random Network
From Greaves and Ngai, 1995

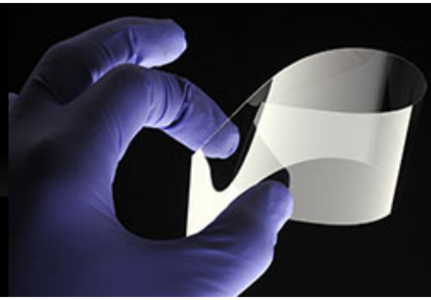


We propose a new version:
Compensated Modified Random
Network

Na and K are in different structural positions

$\Rightarrow$ Two different networks

$\Rightarrow$ Non random mixing



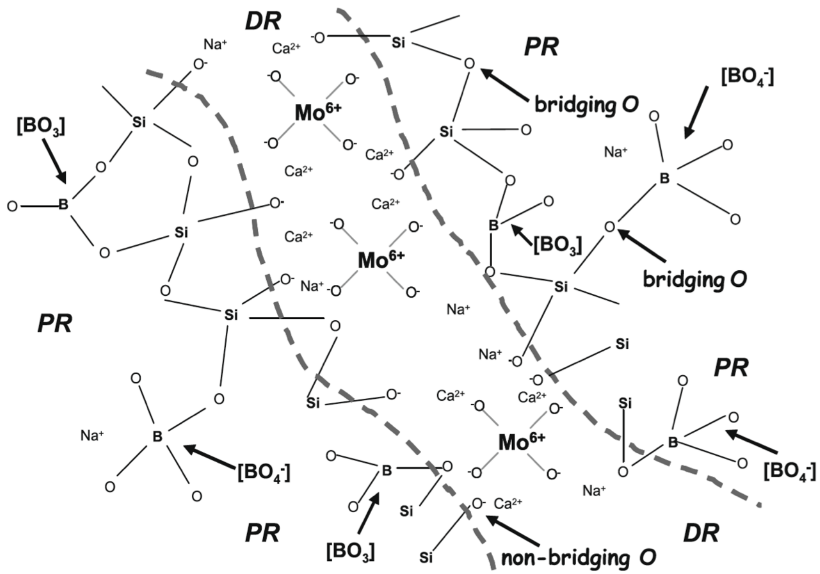
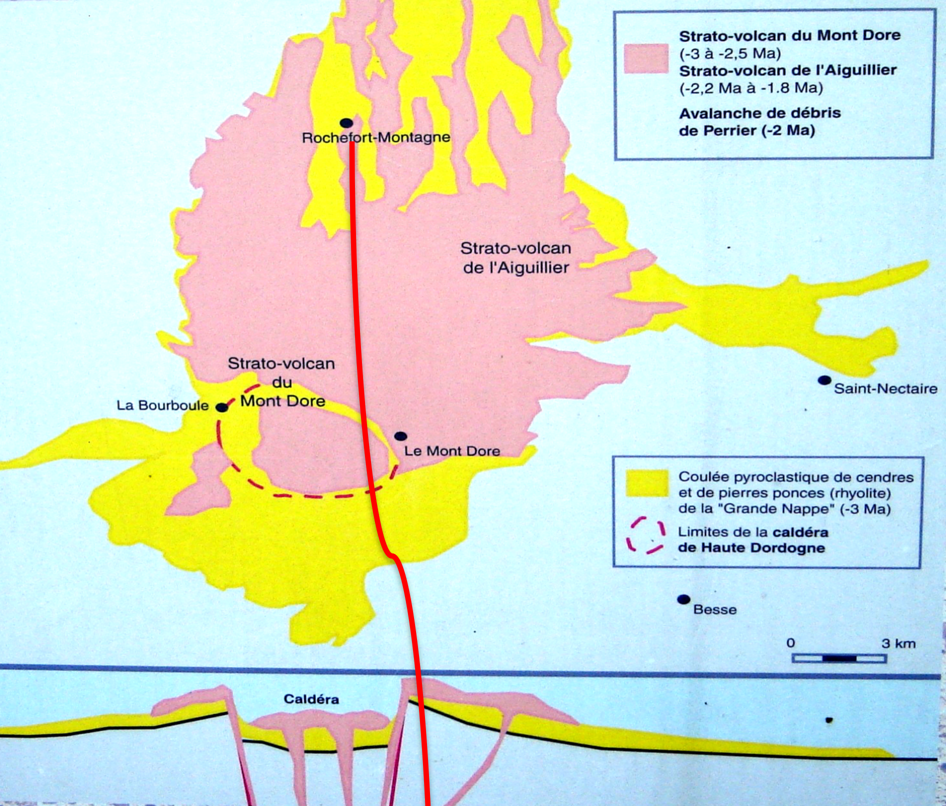


Fig. 1. Schematic representation of the structure of a soda-lime borosilicate glass containing molybdenum according both to Mo EXAFS results reported in literature [1,7,18] and to the modified random network model of the structure of modified silicate glasses [41]. In this figure are shown: $(MoO_4)^{2-}$ entities no directly connected to the borosilicate network but located in depolymerized regions of the glass structure, SiO_4 tetrahedra, BO_4 tetrahedral units that can be charge compensated by Na^+ or Ca^{2+} cations, BO_3 triangles. Examples of bridging oxygen atoms (BOs) and non-bridging oxygen atoms (NBOs) are shown. The possible presence of Si and B in the neighborhood of MoO_4^{2-} units – as second neighbors of the Na^+ or Ca^{2+} cations that charge compensate the molybdate units – is proposed in the figure. DR: depolymerized regions (i.e. regions rich in both NBOs and $Na^+ + Ca^{2+}$ cations); PR: polymerized regions (i.e. NBOs-poor regions). The dotted lines separate DR and PR regions.

Caurant D., Majèrus O., Fadel E., Quintas A., Gervais C., Charpentier T., Neuville D.R., (2010) Structural investigation of borosilicate glasses containing MoO3 by MAS NMR and Raman spectroscopy. Journal of Nuclear Materials, 396, 94-101.

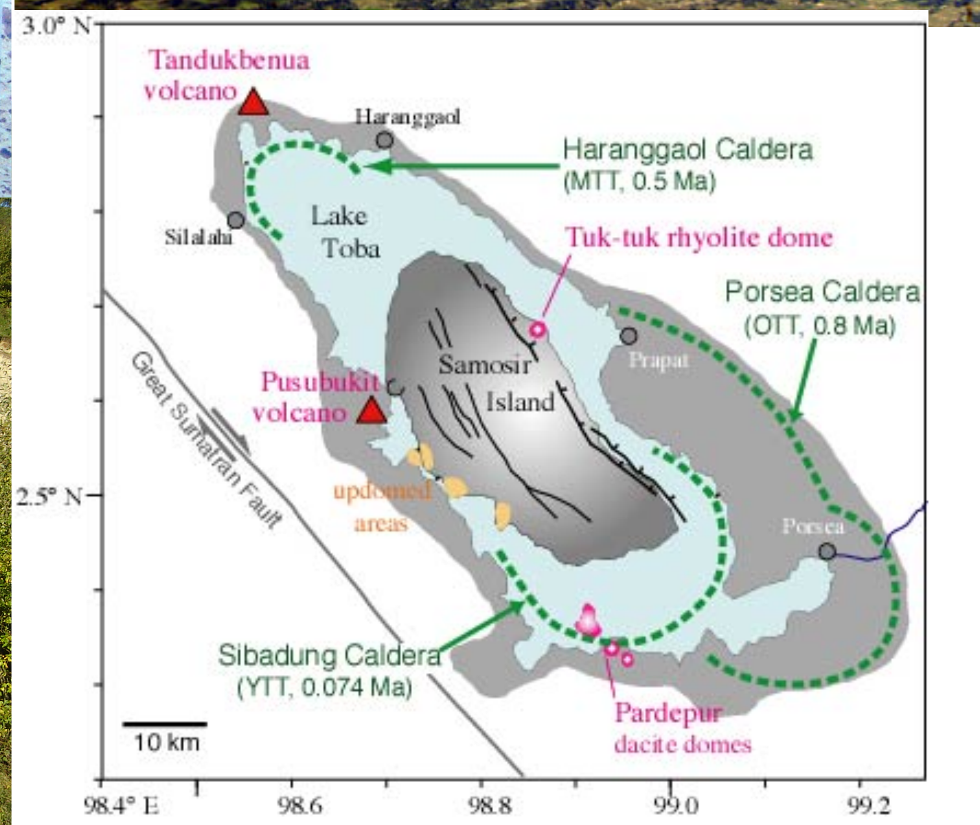
Chaiten

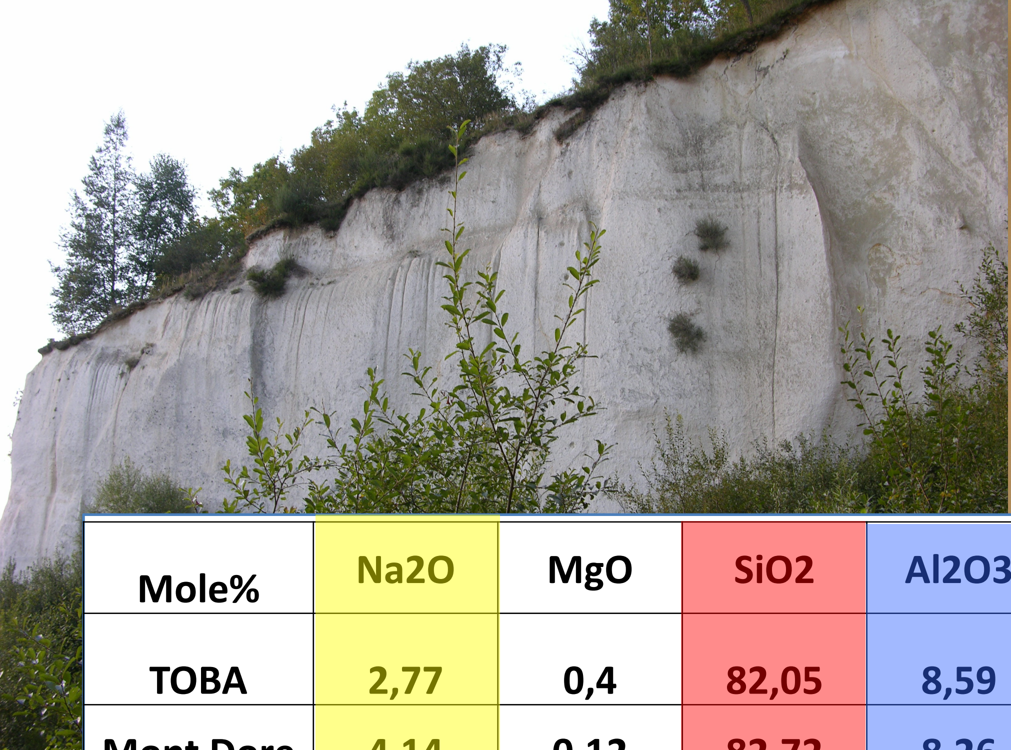
Nyiracongo

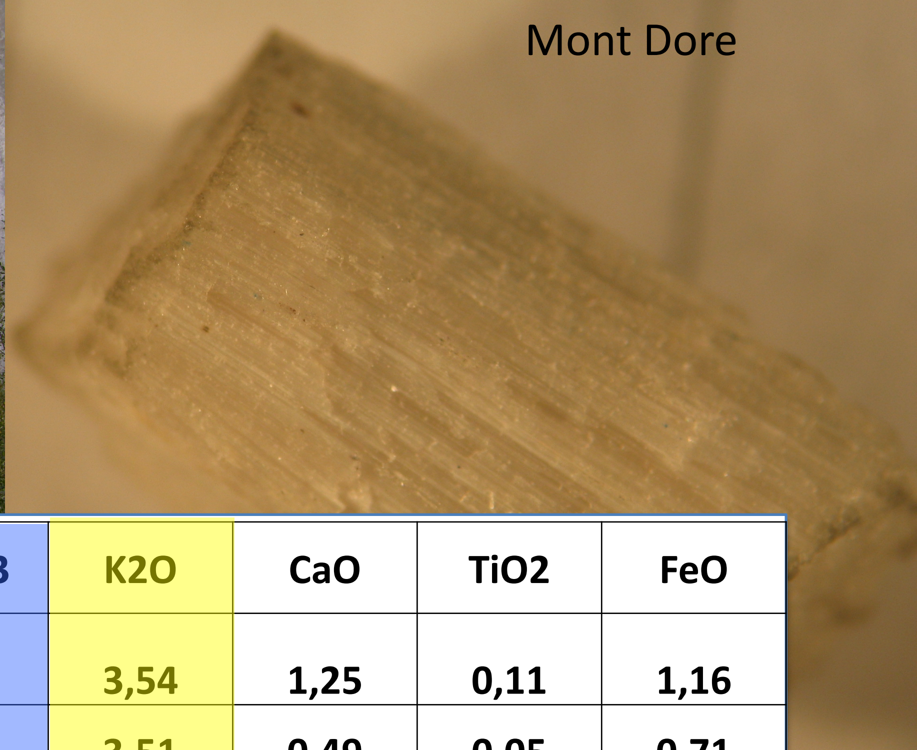

Strato-volcan du Mont Dore
(-3 à -2,5 Ma)
Strato-volcan de l'Aiguillier
(-2,2 Ma à -1.8 Ma)
Avalanche de débris
de Perrier (-2 Ma)
Rochefort-Montagne
Strato-volcan
de l'Aiguillier
Strato-volcan
du
Mont Dore
La Bourboule
Le Mont Dore
Saint-Nectaire
Coulée pyroclastique de cendres
et de pierres ponces (rhyolite)
de la "Grande Nappe" (-3 Ma)
Limites de la caldéra
de Haute Dordogne
Besse
0
3 km
Caldéra


TOBA Indonesia

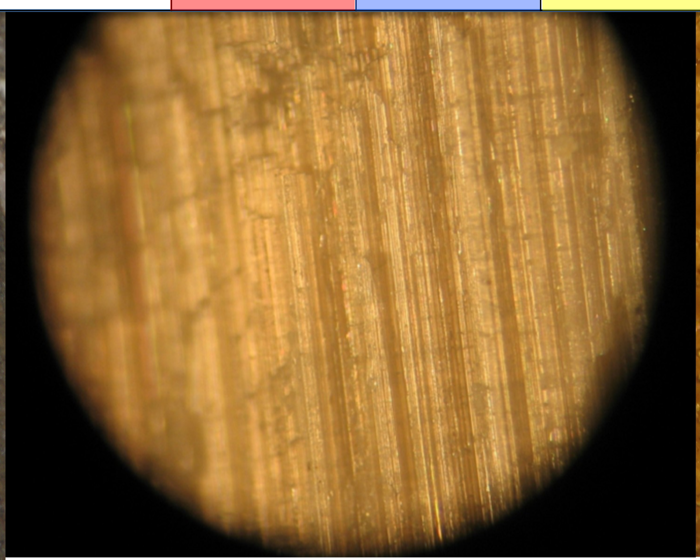

MONT DORE
France

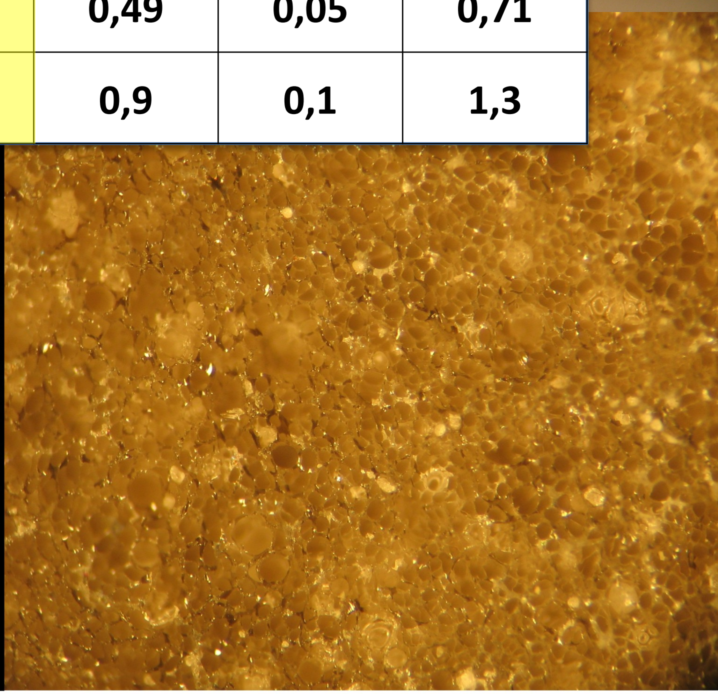

3.0° N
Tandukbenua
volcano
Haranggaol
Haranggaol Caldera
(MTT, 0.5 Ma)
Silalahi
Lake
Toba
Tuk-tuk rhyolite dome
Porsea Caldera
(OTT, 0.8 Ma)
Prapat
Samosir
Island
Pusubukit
volcano
Great Sumatran Fault
updomed
areas
2.5° N
Porsea
Sibadung Caldera
(YTT, 0.074 Ma)
Pardepur
dacite domes
10 km
98.4° E
98.6
98.8
99.0
99.2





Mole%	Na2O	MgO	SiO2	Al2O3	K2O	CaO	TiO2	FeO
TOBA	2,77	0,4	82,05	8,59	3,54	1,25	0,11	1,16
Mont Dore	4,14	0,12	82,72	8,26	3,51	0,49	0,05	0,71
Yellowstone	3,3	0,2	83,7	7,5	3	0,9	0,1	1,3



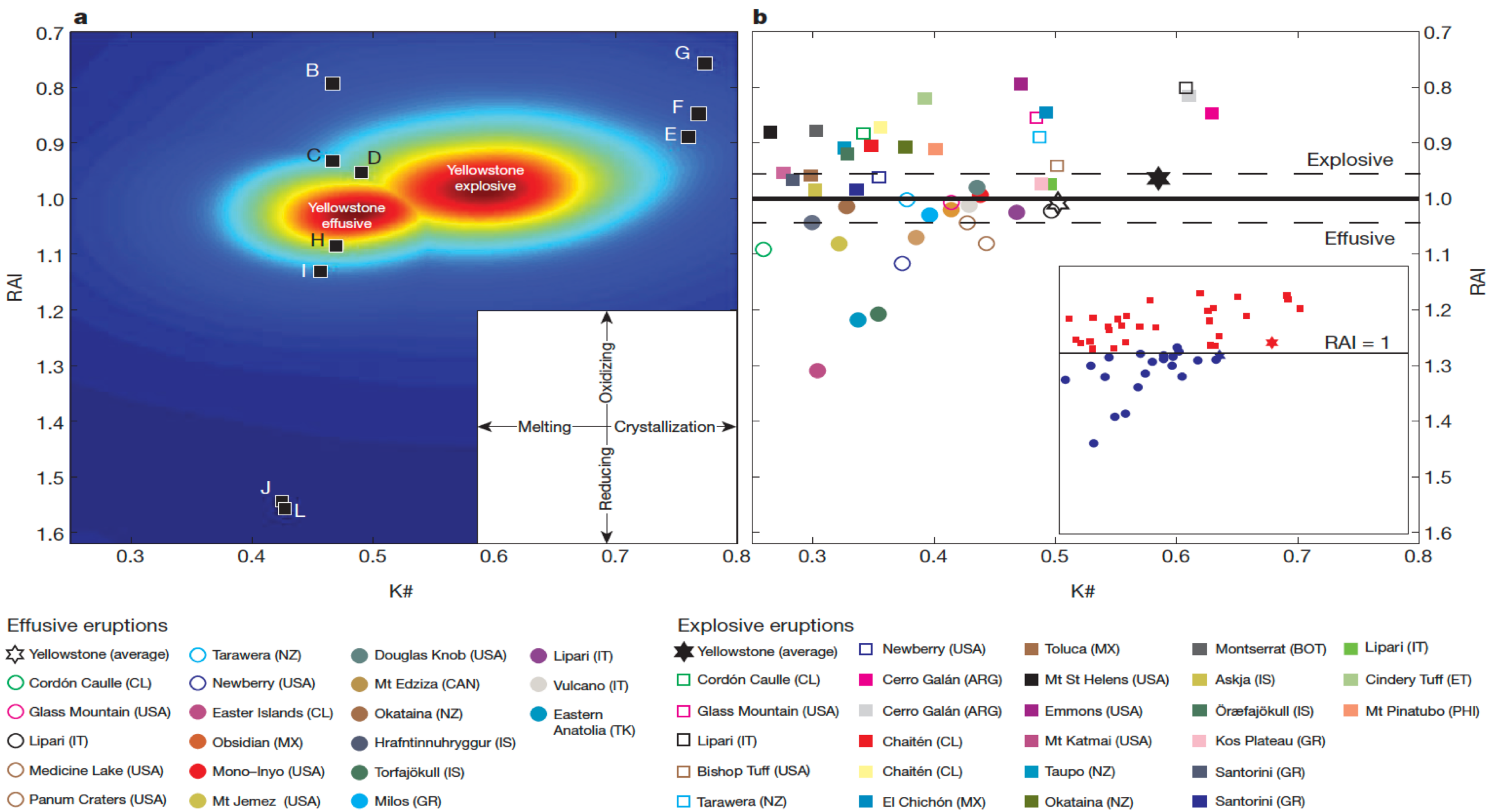


LETTER

doi:10.1038/nature24488

A compositional tipping point governing the mobilization and eruption style of rhyolitic magma

D. Di Genova[1,2], S. Kolzenburg[2], S. Wiesmaier[2], E. Dallanave[2], D. R. Neuville[3], K. U. Hess[2] & D. B. Dingwell[2]



- ✓ Zachariasen model … 1er approximation : disorder long range
- ✓ Residual entropy at0K = configuration entropy
- ✓ Configuration entropy = image of the glass and liquid
- ✓ Ideal mixing for Ca, Mg, Zn and also Al and Si
- ✓ Non ideal mixing for Na, Ca, more generally for all alkali and earth-alkaline
- ✓ => Compensated continuous Random Network : Greaves 1981
- ✓ **=> new version: Compensated Modified Random Network**
- ✓ **=> huge impact for material and Earth Sciences**